

# ***NERL/ERD Publications***

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**Jan 1, 2002 - Dec 31, 2002**

***Presented Published***

## ***ABSTRACT/ORAL***

Bird, S.L., Harrison, J., and Exum, L.R. Screening to identify and prevent urban storm water problems: estimating impervious area accurately and cheaply. Presented at: National Water Quality Monitoring Conference, Madison, WI, May 20-23, 2002.

5/20/2002

***Contact:*** Sandra L. Bird

***Abstract:*** Complete identification and eventual prevention of urban/suburban water quality problems pose significant monitoring challenges. Uncontrolled growth of impervious surfaces (roads, buildings and parking) causes detrimental hydrologic changes, stream channel erosion, habitat degradation and severe impairment of aquatic life. Aerial photography (digital orthophoto quarter quadrangles - DOQQ's), sampled statistically using desktop GIS tools, were used to evaluate impervious area estimates based on available landscape data including categorized land cover data (National Land Cover Data - NLCD), block level census data, and road networks. The wide area estimation techniques provided: 1) cheap estimates of impervious cover with known accuracy at the watershed and sub-watershed scales, 2) a comprehensive regional ranking of waters likely impaired by urban storm water, and 3) characterization of imperviousness changes over time. These screening results can guide in-situ monitoring to confirm problems, aid 303(d) listing and development, provide sound information to energize local decision makers, and promote protection and restoration of urban streams.

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*Presented Published*

Bouchard, D.C. Using methanol-water systems to investigate phenanthrene sorption-desorption on sediment. Presented at: 223rd American Chemical Society National Meeting, Orlando, FL, April 7-11, 2002.

4/7/2002

**Contact:** Dermont Bouchard

**Abstract:** Sorption isotherm nonlinearity, sorption-desorption hysteresis, slow desorption kinetics, and other nonideal phenomena have been attributed to the differing sorptive characteristics of the natural organic matter (NOM) polymers associated with soils and sediments. A conceptualization of NOM sorptive character that has appeared frequently in the literature recently draws on synthetic polymer chemistry concepts in describing NOM as a rubbery/glassy polymer where sorption in the expanded NOM rubbery domain occurs by partitioning, which is linear with solute concentration and rapid; and where sorption in the more condensed NOM glassy domain is nonlinear and characterized by slow sorption-desorption kinetics (1-3). This conceptual model has been given some credence in that naturally occurring humic substances have also been described as having both condensed and expanded regions (4), and humic polymers molecular weights are similar to those of many synthetic polymers. If NOM behaves similarly (with respect to sorption) to more homogeneous synthetic polymers, with both a rubbery and glassy nature, then one would expect that organic solvents would have similar effects on the sorptive properties of both NOM and synthetic polymers. The objective of the research presented here is to test this hypothesis; i.e., to determine if solute sorption on NOM in the presence of an organic solvent is consistent with the rubbery-glassy polymer construct. Methanol was selected for this study because of the large database for its use in soils, its presence in the polymer science literature, and because of its high dissolution capacity in NOM (5). The batch sorption-desorption techniques used were similar to those used previously by the author (6). The Upper Call's Creek sediment was air-dried and passed through a 1-mm sieve prior to use, this fraction having a total organic carbon content of 0.75% and being dominated by the sand and silt fractions with <1% clay content. All aqueous solution components were 0.01N in CaCl<sub>2</sub> and contained 200 mg/L sodium azide as a biocide. The batch reactors were 20-mL borosilicate glass vessels with foil-lined caps. Based on the anticipated sorption magnitude, differing amounts of air-dry sediment were weighed into batch reactors. The amount of phenanthrene sorbed to the sediment ( $S$ , nmol/g) was determined by the difference between the initial solution concentration ( $C_0$ , nmol/ml) and the equilibrium solution concentration ( $C_e$ , nmol/ml). The equilibrium sorption coefficient ( $K$ ) was defined as the slope of the  $C_e$  vs  $S$  plots. The linear sorption model was used in this study as it described the data quite well (a fairly narrow range of  $C_0$  was used) and because it allows direct comparison of  $K$  values. To close the phenanthrene mass balance at the end of the desorption study, the sediment was extracted with methanol at 55°C using a method similar to that of Huang and Pignatello [7]. One sorption and two desorption isotherms are presented in Figure 1. The lower two isotherms represent phenanthrene sorption-desorption in aqueous systems. As has often been noted in prior studies, the system exhibited some hysteresis with sorption magnitude being greater during the desorption phase than in the sorption phase. Of particular interest, however, is the upper isotherm for the treatments that were equilibrated with phenanthrene in a 40% (v/v) methanol/water solution, and then desorbed with an aqueous solution. The sorption coefficient in this treatment was nearly double that of the purely aqueous treatments. These results were also corroborated by studies conducted at 60% methanol/water concentrations. The higher degree of phenanthrene retention in the mixed solvent equilibrated system may have been due to methanol induced relaxation of the rigid structure of glassy NOM domains, forcing transit to a more rubbery state that acts more like a partitioning medium. Since sorption in the glassy domain is slow, and partitioning is known to be rapid, the end result is faster sorption kinetics in the rubbery domain. Hence, the sorption coefficient in the mixed solvent equilibrated system may reflect a sorption measurement more characteristic of longer solute-sorbent contact times than the 1-week equilibrations used in this study. All of the above studies were performed using 3H-labelled phenanthrene. After the initial 3H phenanthrene desorption step, 14C-labelled phenanthrene in aqueous solution was added. This procedure constituted the second 3H-phenanthrene desorption step (a total of three were performed) and the initial 14C-phenanthrene sorption step used to determine the reversibility of the postulated NOM changes elicited by the methanol. Results indicated that any changes in the NOM sorptivity were at least partially reversible as the 14C-phenanthrene sorption-desorption isotherms (not shown) exhibited somewhat greater phenanthrene retention than the purely aqueous systems, but significantly less retention than the mixed solvent equilibrated systems. Finally, extraction recoveries to close the phenanthrene mass balance at the end of the desorption studies were all >87%, thus demonstrating the ultimate reversibility of the sorption-desorption process, and also, consistency with the concept of a reversible and deformable NOM phase.

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Bouchard, D.C. Atrazine desorption kinetics from a fresh-water sediment. Presented at: 54th Southeast Regional Meeting of the American Chemical Society, Charleston, SC, November 13-16, 2002.

11/13/2002

**Contact:** Dermont Bouchard

**Abstract:** Research has shown that the sorption and desorption of neutral organic compounds to soils and sediments occurs in two stages, with an initial rapid sorption/desorption phase (usually less than an hour) followed by a slower phase that can last for several months to years for very high  $K_p$  solute-sorbent combinations. Hence, the popularity of various "two-step" or "two-domain" conceptualizations and mathematical models for describing solute sorption and desorption. In this study atrazine was incubated with a sediment from a small north Georgia stream for 26 weeks and then desorbed in a sediment column system operated under saturated flow conditions. Atrazine desorption from the column under different experimental parameters was described using a two-step first-order kinetic model. In addition, atrazine desorption from the aged sediment was compared to atrazine transport in the sediment under short-term exposure conditions.

Molinero, J., and Burke, Jr., R.A. Assessing non-point sources of nitrogen to small streams in the South Fork Broad River watershed (Georgia, USA). Presented at: VII International Congress of Ecology, Seoul, Korea, August 11-18, 2002.

8/11/2002

**Contact:** Roger A. Burke

**Abstract:** The National Land Cover Data (NLCD) is a land cover classification derived from Landsat Thematic Mapper satellite data collected in the early to mid-1990s. In this work, land use coverages calculated from the NLCD database are used to assess the impact of non-point sources on the nitrogen concentrations in small headwater streams. Dissolved organic nitrogen (DON) and particulate nitrogen (PN), which are not included in most nutrient studies, are also considered in this work. The Broad River is located in northeast Georgia and flows from the Appalachian mountains to its confluence with the Savannah River at the Clarks Hill/Strom Thurmond reservoir. The South Fork Broad River (SFBR) is a 128 km length tributary to the Broad River located in the southwest part of its watershed. The SFBR watershed is about 556 km<sup>2</sup> and it is primarily rural and remains in a largely natural state. Agriculture and pasture land are the main uses throughout the valley and there are also some managed forests. Industrial use in the watershed is limited to a few granite quarries. Twelve headwater watersheds ranging from 0.5 to 3.4 km<sup>2</sup> were selected. Percentages of forested land, agricultural and pasture land, residential areas, wetlands and open water surfaces within the watershed were calculated from the NLCD database. Water samples were collected monthly from November 2001 to March 2002 at the outlet of each watershed. Samples for dissolved inorganic and organic nitrogen were filtered with 0.45  $\mu$ m membrane filters. Oxidized nitrogen (nitrate + nitrite) was determined by UV detection. DON and PN were determined by persulfate digestion followed by UV detection. Ammonia was determined with an Accumet ammonia electrode. Linear models relating land uses to the nitrogen concentrations in the streams developed by step-wise regression. The lowest total nitrogen (TN) concentrations were found in forested streams (0.310-0.318 mg N/l). TN concentrations were high in streams draining developed areas (0.606-2.643 mg N/l) and pasture and agricultural land (1.334-2.623 mg N/l). Finally, streams in watersheds with mixed land uses showed intermediate TN concentrations (0.597-1.232 mg N/l). Up to 70 % of the TN in streams draining residential areas was dissolved inorganic nitrogen (DIN). In contrast, streams in forested watershed had less nitrogen (45 %) in inorganic form and about twice more nitrogen (45 %) in organic form than streams in residential areas. Streams in agricultural and pasture land dominated watersheds had about twice more nitrogen (15 %) in particulate form than in either forested or residential watersheds. The amount of forested land within the watershed was the best predictor to the concentrations of the different forms of nitrogen in the streams. These observations support that land uses within the watershed largely influences both nitrogen concentrations and forms in stream water. Also, the impact of land uses on nitrogen concentrations in streams at a local scale can be assessed using data derived from the NLCD database.

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Burke, Jr., R.A., and Molina, M. Use of fatty acid stable carbon isotope ratio to indicate microbial carbon source in tropical soils. Presented at: 3rd Annual International Conference on Application of Stable Isotope Techniques to Ecological Studies, Flagstaff, AZ, April 28-May 1, 2002.

4/28/2002

**Contact:** Roger A. Burke

**Abstract:** We use measurements of the concentration and stable carbon isotope ratio of individual microbial phospholipid fatty acids (PLFAs) in soils as indicators of live microbial biomass levels, broad microbial community structure, and microbial carbon source. For studies of soil organic matter (SOM) cycling, the PLFA d13C technique is easiest to apply in ecosystems that have undergone a vegetation change (e.g. from C3 to C4 photosynthetic pathway) at known times in the past. Using principal components analysis (PCA) of the PLFA profiles, we were able to detect differences in microbial community structure related to soil type (Oxisol vs Andisols), agricultural management (forest vs pasture vs sugarcane), and soil depth. The PLFA stable carbon isotope ratio measurements showed that the soil microbial community living in the very old, relatively carbon-poor Oxisol site switched over to C4 carbon under sugarcane cultivation much more quickly (half life about 10 years) than did the sugarcane soil microbial communities in the much younger, carbon-rich Andisol sites (half life about 40 years).

Burke, Jr., R.A., and Molinero, J. Nitrous oxide concentrations in small streams of the Georgia Piedmont. Presented at: American Society of Agronomy-Crop Science Society of America-Soil Science Society of America Annual Meeting, Indianapolis, IN, November 10-14, 2002.

11/10/2002

**Contact:** Roger A. Burke

**Abstract:** We are measuring the dissolved nitrous oxide concentration in 17 headwater streams in the South Fork Broad River, Georgia watershed on a monthly basis. The selected small streams drain watersheds dominated by forest, pasture, developed, or mixed land uses. Nitrous oxide concentrations vary widely from 10 nM (atmospheric equilibrium concentration) to nearly 80 nM among the streams. Our measurements to date imply that many of the streams have nearly constant dissolved nitrous oxide concentrations regardless of season. Some of the streams have fluctuating nitrous oxide concentrations but the variations are not obviously related to temperature. Overall, the streams draining watersheds dominated by developed land use have the highest dissolved nitrous oxide concentrations although the difference is statistically significant only for comparisons with the forest and mixed land use watersheds. Also, the streams draining watershed dominated by pasture have significantly greater nitrous oxide concentrations overall than streams draining forested watersheds. These results suggest that small streams could be a significant source of nitrous oxide to the atmosphere in some watersheds.

Garrison, A.W., Jones, W.J., and Avants, J. Use of capillary electrophoresis to measure the enantioselective transformations of chiral environmental pollutants. Presented at: EnviroAnalysis 2002, Toronto, Canada, May 27-31, 2002.

5/27/2002

**Contact:** Arthur W. Garrison

**Abstract:** The enantiomers of chiral pollutants have identical physical and chemical properties but usually react selectively with enzymes or other chiral molecules. This enantioselectivity results in different rates of microbial transformation and differences in toxicity of the 2 (or more) enantiomers. To make more accurate risk assessments, it is necessary to understand the relative persistence and effects of the enantiomers; it follows that this understanding depends upon the ability to separate them. Enantiomeric separation can be accomplished by the use of chiral columns in GC and HPLC, and by chiral selectors in capillary electrophoresis (CE). This presentation will describe techniques for enantiomer separation by CE, and show applications to environmental problems. For example, we have applied CE with cyclodextrin selectors to the analysis of a variety of soil samples spiked with an organophosphorus pesticide (crufomate) and a phenoxyacid herbicide (dichlorprop) to follow their enantioselective microbial transformation kinetics. We have also used CE to follow the enantioselective loss of bromochloroacetic acid spiked into several surface water samples, which showed that in most cases the same enantiomer degraded fastest. Current studies involve CE to follow the loss of the enantiomers of dyfonate (an OP pesticide), imazaquin (an imidazolinone herbicide), and metalaxyl (an acylanilide fungicide) in soil slurries. CE, although less sensitive than GC or HPLC, has particular advantages that make it viable for following the transformation of chiral pollutants in benchtop experiments where the analyte can be dosed at a reasonably high concentration.

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*Presented Published*

Lehmle, H.J., Price, D.J., Garrison, A.W., and Robertson, L.W. Distribution of PCB 84 enantiomers in C56BL/6 mice. Presented at: 2nd PCB Workshop: "Recent Advances in the Environmental Toxicology and Health Effects of PCBs", Brno, Czech Republic, May 7-11, 2002.

5/7/2002

**Contact:** Arthur W. Garrison

**Abstract:** At room temperature, nineteen of the 209 possible PCB congeners exist as pairs of stable rotational isomers that are enantiomeric to each other. A racemic mixture of each of these PCB atropisomers is present in technical mixtures, thus raising concerns about enantioselective distribution, metabolism, and disposition processes. An understanding of these processes in combination with knowledge of different biological effects of pure PCB enantiomers is necessary to calculate the overall risk of exposure to chiral PCB congeners. This study investigates the distribution and enantiomeric fractions (EF) of PCB 84 in several organs in uninduced female C57BL/6 mice. Methods: PCB 84 (EF = 0.513 ± 0.003) was injected intraperitoneally (600 mmol/kg body weight), and organs (liver, brain, lung, heart, spleen and kidney) were removed after three and six days, respectively. The PCB enantiomers were separated by GC on a chiral phase composed of 20% tert-butylidimethylsilylated- $\beta$ -cyclodextrin (BGB 172 chiral column, BGB Analytik AG, Anwil, Switzerland) and detected with a mass selective detector. With this chiral phase, the (-)-enantiomer of PCB 84 elutes first. Resolution of the enantiomers of PCB 84 was  $R = 0.8$  ( $n = 3$ ). Because there were no interfering peaks in the samples, this ratio was sufficient for the determination of enantiomer fractions. Results: The EFs in brain, liver, lung and heart were significantly different from the racemic PCB 84 standard at days three and six, with an enrichment of (+)-PCB 84 in all four tissues. A significant enrichment of (+)-PCB 84 in the kidney was observed for day six. No significant difference was observed for the spleen. Tissue EFs for the brain showed the highest EF, whereas the EFs in the spleen were almost identical with the PCB 84 standard. The EFs did not change significantly between day three and six. Conclusions: There is a significant enrichment of (+)-PCB 84 in several tissues (brain, liver, lung, heart and kidney) three and/or six days after administration of a racemic mixture of PCB 84. This enrichment may be due to enantioselective metabolism in these tissues and/or enantioselective distribution or disposition of PCB 84. Our findings suggest that the risk assessment of PCB 84 and, possibly, other atropisomeric PCB congeners should take enantioselective processes into account.

Ulrich, E.M., Wong, C.S., Rounds, S.A., Van Metre, P.C., Wilson, J.T., Garrison, A.W., and Foreman, W.T. Chiral chlordanes signatures in USGS National Water-Quality Assessment Program sediment samples. Presented at: 23rd Annual Society of Environmental Toxicology and Chemistry Meeting, Salt Lake City, UT, November 16-20, 2002.

11/16/2002

**Contact:** Arthur W. Garrison

**Abstract:** More than 260 important environmental contaminants are chiral (having structures that are nonsuperimposable mirror images). Although enantiomer pairs have identical physical-chemical properties, their toxicity, biodegradation, and environmental fate often are different. Cyclodextrin gas chromatography combined with electron-capture, negative ionization mass spectrometry was used to determine the chiral characteristics of chlordanes components in sediment. Enantiomer fractions [EF = area (+) enantiomer / sum of (+) and (-) areas] were used to determine if biological degradation had occurred in surficial and suspended-sediment samples, and if there was a trend with depth in sediment cores. Suspended-sediment samples showed the most change from a racemic signature, possibly indicating greater bioavailability of chlordanes associated with the suspended fraction. Surficial sediments contained evidence of biodegradation because of the presence of nonracemic EFs [not equal to 0.50; cis-chlordane (CC) = 0.502 - 0.62; trans-chlordane (TC) = 0.473 - 0.54; exo-heptachlor epoxide (HEPX) = 0.60 - 0.682]. The EF of HEPX in surficial sediment agrees with those found in soil, indicating agricultural soil as a likely source. At four core sites, EFs were close to racemic for TC and CC, with the greatest deviations from racemic observed in the top (recently deposited) core segment. In general, TC EFs were less than 0.5 and tend to increase slightly with depth, while the opposite was true for CC. These results suggest that little biodegradation has occurred in the sediment core, and that historical concentration profiles should be unaltered by biological degradation processes.

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*Presented Published*

Lee, C.M., Pakdeesusuk, U., Freedman, D.L., Coates, J.T., Garrison, A.W., and Elzerman, A.W. PCBs in Lake Hartwell, SC, headwaters of the Savannah River basin. Presented at: 54th Southeast Regional Meeting of the American Chemical Society, Charleston, SC, November 13-16, 2002.

11/13/2002

**Contact:** Arthur W. Garrison

**Abstract:** Contamination due to polychlorinated biphenyls (PCBs) was discovered in the mid-1970s in the fish and sediments of Lake Hartwell, a U.S. Army Corps of Engineers reservoir on the border of South Carolina and Georgia that was formed from the Seneca and Tugaloo Rivers. Research by universities, state agencies, and consulting firms has revealed much about the distribution and behavior of PCBs in this reservoir system. The latest findings include the presence of on-going reductive dechlorination and the role of enantioselective transformations of PCBs by microorganisms eluted from the sediments of Lake Hartwell. Field data that compares 1987 cores with 1998 cores as well as results from microcosms support continuing removal of chlorine at specific locations and depths. Chiral analyses provide insight into microbial reductive dechlorination and may serve as a surrogate parameter for biodegradation. These findings will be discussed in the historical context of the long-term work.

Laniak, G.F. Software system design and implementation for environmental modeling: a MOU working group. Presented at: Interagency Conference on Hydrology, Las Vegas, NV, July 28-August 1, 2002.

7/28/2002

**Contact:** Gerard F. Laniak

**Abstract:** A workgroup was formed in conjunction with a formal Memorandum of Understanding (MOU) among six Federal Agencies to pursue collaborative research in technical areas related to environmental modeling. Among the primary objectives of the MOU are to 1) provide a mechanism for the cooperating Federal Agencies to pursue a common technology in multimedia environmental modeling with a shared scientific basis, 2) reduce redundancies and improve the common technology through exchange and comparisons of multimedia environmental models, software and related databases, 3) exchange information related to multimedia environmental modeling tools and supporting scientific information for environmental risk assessments, protocols for establishing linkages between disparate databases and models, and development and use of a common model-data framework, and 4) facilitate the establishment of working partnerships among the cooperating Federal Agencies' technical staff in order to enhance productivity and mutual benefit through collaboration on mutually-defined research studies. In direct support of the goals of the MOU this workgroup focuses specifically on the computer software infrastructure necessary to support state-of-the-science environmental systems analyses. It is important to differentiate the software infrastructure from the science-based environmental modeling components contained therein. The infrastructure represents a set of software development standards and tools that facilitate the development and application of environmental models. It specifically does not include or address the science embedded within the models and associated databases. The infrastructure is important at three levels: the standards level, the component level and the integrated environmental assessment level. Software development standards, in this context, define requirements and protocols for designing and implementing software such that it can execute within a larger system in coordination with other, complementary, modeling software. The standards are applied at the component and integrated analysis levels. The second level of infrastructure includes software components for managing data access, transfer, and analysis. These components facilitate the integrated use of the science-based models and databases included in the modeling system. The third level relates to the automated organization and execution of collections of modeling components for the purpose of performing integrated assessments in support of environmental research and organizational decision making. This presentation will describe, in some detail, the formation of the workgroup, its members, the mechanics of the collaborative relationship established to date, and the specific technical activities currently being pursued.

Loux, N.T., and Washington, J.W. Errors in applying low ionic-strength activity coefficient algorithms to higher ionic-strength aquatic media. Presented at: 223rd American Chemical Society National Meeting, Orlando, FL, April 7-11, 2002.

4/7/2002

**Contact:** Nicholas T. Loux

**Abstract:** The toxicological and regulatory communities are currently exploring the use of the free-ion-activity (FIA) model both alone and in conjunction with the biotic ligand model (BLM) as a means of reducing uncertainties in current methods for assessing metals bioavailability from aquatic media. While most practitioners would support the desirability of this objective, several technical questions remain to be addressed in achieving this goal. The free ion activity ( $a_{Mez+}$ ) of an ion in solution is composed of the product of the concentration of the ion ( $[Mez+]$ ) times the respective activity coefficient ( $g_{Mez+}$ ); i.e.,  $a_{Mez+} = [Mez+]g_{Mez+}$ . The activity coefficient represents the excess free energies associated with the interactions of the host ion with other ions and/or water molecules in solution. In sufficiently dilute salt solutions,  $g_{Mez+}$  equals 1.

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*Presented Published*

Loux, N.T., Collette, T.W., and Washington, J.W. An alternative method for relating macroscopic to microscopic acidity constants with zwitterionic species. Presented at: 223rd American Chemical Society National Meeting, Orlando, FL, April 7-11, 2002.

4/7/2002

**Contact:** Nicholas T. Loux

**Abstract:** Using the notation of Adams (1916. JACS, 38:1503), zwitterionic microscopic acidity constants defined by:  $k_a = [H^+][+H_3NRCOO^-]/[+H_3NRCOOH]$ ;  $k_b = [H^+][H_2NRCOOH]/[+H_3NRCOOH]$ ;  $k_c = [H^+][H_2NRCOO^-]/[+H_3NRCOO^-]$ ; and  $k_d = [H^+][H_2NRCOO^-]/[H_2NRCOOH]$  are historically related to the experimentally measurable macroscopic acidity constants by:  $K_1 = k_a + k_b$  and  $1/K_2 = 1/k_c + 1/k_d$  (ignoring activity coefficients). These expressions can be viewed as procedures for approximating biprotic systems with a monoprotic formulation. The reader can observe that under conditions where  $k_a \gg k_b$  and  $k_c \gg k_d$ , then  $K_1 \approx k_a$  and  $K_2 \approx k_d$ ; and when  $k_a \approx k_b$  and  $k_c \approx k_d$ , then  $K_1 \approx 2k_a$  (or  $2k_b$ ) and  $K_2 \approx k_c/2$  (or  $k_d/2$ ). We will present evidence that while a monoprotic approximation of a 2 pK system is appropriate under some circumstances, a geometric mean (rather than an arithmetic sum) of the microscopic acidity constants can provide superior accuracy in some applications.

Ekman, D.R., Lorenz, W.W., McCutcheon, S.C., and Wolfe, N.L. Use of serial analysis of gene expression (SAGE) to study genetic responses to the presence of the TNT or RDX by *Arabidopsis thaliana*. Presented at: Sixth International Symposium on Environmental Biotechnology and Fourth International Symposium on Cleaner Bioprocesses and Sustainable Development, Vera Cruz, Mexico, June 9-12, 2002.

6/9/2002

**Contact:** Nelson L. Wolfe

**Abstract:** Phytoremediation is currently being explored for its potential to clean-up of the large number of military sites that have been contaminated by explosives such as 2,4,6-trinitrotoluene (TNT) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). Although some of the enzymes responsible for the metabolism of explosives have been identified, little is known about plant responses to these pollutants at a genetic level. In light of this fact, a comprehensive genomics approach known as SAGE (Velculescu et al. 1995) is now being employed to improve the situation. Using SAGE, genes important in the metabolism of both TNT and RDX will be identified, giving the field a more detailed understanding of the plant mechanisms involved. Like many other genomic techniques (e.g. microarrays, oligo-based gene chips, differential display, etc.), SAGE provides for comparisons of genetic expression between organisms experiencing different stimuli. Thus, comparisons will be made in the genetic expression of plants grown in the presence of either TNT or RDX and in the absence (control). For the true power of the technique to be realized a plant species with a known genome must be utilized and thus the flowering plant *Arabidopsis thaliana* was chosen. Currently, the TNT-SAGE library has been completed and genes are being identified. Prior to the SAGE analysis, the concentration of explosive necessary to produce a response without killing the plants was determined by growing the plants in sterile liquid media (MS media) in a variety of explosive (either TNT or RDX) concentrations. In this way the SAGE analysis will identify genes that the plant is expressing to "deal" with the explosive and not genes that are simply involved in the process of cell death.



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*Presented Published*

Hoehamer, C.F., Mazur, C.S., and Wolfe, N.L. Isolation and partial characterization of an acid phosphatase activity from *Spirodela oligorhiza*. Presented at: Sixth International Symposium on Environmental Biotechnology and Fourth International Symposium on Cleaner Bioprocesses and Sustainable Development, Vera Cruz, Mexico, June 9-12, 2002.

6/9/2002

**Contact:** Nelson L. Wolfe

**Abstract:** An acid phosphatase activity from the aquatic plant *Spirodela oligorhiza* (duckweed) was isolated and partially characterized. *S. oligorhiza* was grown in a hydroponic growth medium, harvested, and ground up in liquid nitrogen. The ground plant material was added to a biological buffer, and after ultrafiltration and differential centrifugation, two cell-free enzyme fractions were prepared, the soluble and membrane. The soluble fraction of enzymes displayed low amounts of inducible acid phosphatase activity, while it was not detected in the membrane fraction. This enzyme activity was further isolated from the extract by salt precipitation and fast pressure liquid chromatography using columns containing Phenyl-sepharose and Resource S cation-exchange matrices. Acid phosphatase activity in the plant extracts was monitored colorimetrically by measuring the hydrolysis of *p*-nitrophenol from the organophosphate substrates, methyl paraxon and *p*-nitrophenolphosphate. The acid phosphatase activity was determined to have a pH optimum of 6.0 at 25 C, and no other cofactors were required for enzyme activity. Zymogram staining techniques using 4-methylumbelliferyl phosphate visualized two acid phosphatase isoforms on nondenatured semi-native SDS-PAGE gels which corresponded to protein bands on gels stained with Coomassie brilliant blue. While only minor contaminants were observed on the protein gels after the cation exchange step, this enzyme(s) will soon be purified to homogeneity and further characterized with respect to its chemical and physical properties. Additionally, a variety of other organophosphate compounds remain to be tested as substrates with this phosphatase to determine not only its substrate specificity, but the overall potential of this plant in pesticide remediation.

Sealock, G.A., and Wolfe, N.L. Uptake and transformation of explosives by eastern cottonwood (*populus deltoides*). Presented at: Sixth International Symposium on Environmental Biotechnology and Fourth International Symposium on Cleaner Bioprocesses and Sustainable Development, Vera Cruz, Mexico, June 9-12, 2002.

6/9/2002

**Contact:** Nelson L. Wolfe

**Abstract:** The explosives 2,4,6-trinitrotoluene (TNT), hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetraazocine (HMX) have been extensively used by the United States military to manufacture munitions. Since World War II, both the commissioning and disposal of weapons at ammunition plants have led to soil, ground, and surface water contamination by these and other recalcitrant pollutants. It has been reported that certain plants have the ability to absorb and transform some explosives from contaminated water. Limited work has been conducted on testing this ability in field-contaminated soils. In this study, Eastern Cottonwood (*Populus deltoides*) was grown both hydroponically and in explosives-contaminated soil which was obtained from the Naval Surface Warfare Center Crane, Indiana (NSWCC). Cottonwood cuttings were cultivated in 2L Erlenmeyer flasks containing a hydroponic nutrient solution spiked with TNT and RDX. The nutrient solution was sampled daily to determine the rate of uptake by following EPA Method 8330. The results showed TNT was removed at a rate ten-fold faster than RDX. When the munitions reached undetectable concentrations in the growth medium, the plants were harvested. Cuttings were also grown in columns containing munitions contaminated soil and harvested weekly for up to eight weeks. Due to high soil concentrations all seedlings displayed signs of growth inhibition. In both studies, TNT, 2-amino-4,6-dinitrotoluene (2-ADNT), 4-amino-2,6-dinitrotoluene (4-ADNT), and RDX were identified in leaf, root, and stem tissues.



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Zepp, R.G., Moran, M.A., White, E., and Stabenau, E. Photochemical and biological degradation of CDOM in waters from selected coastal regions of the Southeastern United States. Presented at: 2002 Ocean Sciences Meeting, Honolulu, HI, February 11-15, 2002.

2/11/2002

**Contact:** Richard G. Zepp

**Abstract:** Biological and photochemical degradation of colored dissolved organic matter (CDOM) were investigated in controlled experiments using waters from southeastern U.S. estuaries, from the Mississippi River plume and Gulf of Mexico, and from the coastal shelf region in the Florida Keys. Results of the experiments generally indicated that photoreaction results in decreases in the absorption and fluorescence of terrestrially-derived CDOM as well as CDOM derived from seagrasses. Changes in both absorption spectra (increased spectral slope coefficients) and excitation-emission spectra (hypsochromic shifts) also were observed. Terrestrially-derived CDOM photoreacts to produce biologically-labile photoproducts (BLPS) that were measured using cumulative bacterial oxygen consumption during post irradiation-incubation as an index. The spectral slopes of apparent quantum yield spectra for BLP production were similar to those observed for carbon monoxide production and BLP production rates in sunlight were of the same order of magnitude as those for direct DIC photoproduction. Comparisons of photobleaching and BLP production rates for terrestrially-derived CDOM in the Mississippi River plume on the Gulf of Mexico surface and for algal-derived CDOM in chlorophyll maxima below the surface indicate that these two primary CDOM sources may have quite different photoreactivity. Photobleaching and BLP production for the algal derived CDOM were significantly slower than for the terrestrially-derived CDOM from two sites in the plume west of the mouth of the Mississippi

Zepp, R.G. Solar UV radiation and aquatic biogeochemistry. Presented at: Ozone Depletion over the Southern Ocean Workshop, Dunedin, New Zealand, February 22, 2002.

2/22/2002

**Contact:** Richard G. Zepp

**Abstract:** During the past decade significant interest has developed in the influence of solar UV radiation on biogeochemical cycles in surface waters of lakes and the sea. A major portion of this research has focused on photoreactions of the colored component of dissolved organic matter, referred to as CDOM. Photodegradation of CDOM contributes to loss of its UV and visible absorbance and fluorescence. Such "photobleaching", through interactions with climate-sensitive processes such as stratification, enhances the penetration of harmful UV-B radiation into surface waters and can influence the remote sensing of ocean color. In addition to these spectral effects, photoreactions of CDOM alter its biological availability and isotopic composition. Photochemical reactions in surface waters also enhance the cycling of metals such as iron, manganese, copper, and mercury, and result in the direct production of carbon dioxide, carbon monoxide, volatile hydrocarbons, nitrogen oxides, and sulfur-containing gases. This talk will use selected case studies to illustrate approaches that are being used to investigate these intriguing photoreactions in the laboratory and field.

Kisselle, K., Zepp, R.G., Burke, Jr., R.A., Pinto, A., and Bustamante, M. NO<sub>x</sub> and CO emissions from soil and surface litter in a Brazilian savanna. Presented at: 2nd Science Meeting for the Large Atmosphere and Biosphere in Amazonia (LBA), Manaus, Brazil, July 7-10, 2002.

7/7/2002

**Contact:** Richard G. Zepp

**Abstract:** Land clearing and burning in the tropics often results in increased solar irradiation of soil and surface organic matter. This increased light exposure and surface heating may impact the emissions of nitrogen oxides (NO<sub>x</sub>) and carbon monoxide (CO), trace gases that play an important role in tropospheric chemistry. Our objective in this study was to quantify the effect of light on these trace gas emissions at sites located in the Cerrado (savanna) in central Brazil. Two native vegetation types (cerrado sensu stricto and campo sujo) with or without recent burning, and a pasture site were studied. Gas measurements were made in the field using either clear, or covered (opaque), Pyrex chambers sealed on the soil surface. Laboratory studies of surface litter allowed CO emission measurements of leaf litter from several species while controlling the light wavelength and intensity and the temperature. Field NO<sub>x</sub> flux measurements using clear chambers were higher than when using opaque chambers (approximately 4-7 times higher in burned sites; 2 times higher in the unburned native grassland and pasture). Immediately after burning, CO emissions from soils and charred surface organic matter increased in the cerrado, where 30 days after the fire, daytime CO emissions were over 10-fold higher than those from the unburned cerrado (812.8 x 10<sup>9</sup> molecules cm<sup>-2</sup> s<sup>-1</sup> vs. 76.8 x 10<sup>9</sup> molecules cm<sup>-2</sup> s<sup>-1</sup>). The increase in CO production occurred both in light and dark chambers, suggesting that the fire created thermally-reactive precursors.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Sawunyama, P., and Bailey, G.W. Structures and binding energies of methyl tert-butyl ether-water complexes. Presented at: 223rd American Chemical Society National Meeting, Orlando, FL, April 7-11, 2002.

4/7/2002

**Contact:** George W. Bailey

**Abstract:** Methyl tert-butyl ether (MTBE) is a well-known environmental contaminant owing to its high solubility in water. Since the early 1990s, MTBE has been added to gasoline to improve air quality in some metropolitan areas of the United States. Improved air quality was, however, achieved at the expense of MTBE tainted water. MTBE from leaking underground gasoline tanks, urban runoff, boats, etc., has been contaminating surface water and ground water in the very areas MTBE use was supposed to improve air quality. Molecular association between MTBE and water is predominantly via hydrogen bonding with water acting as the hydrogen bond donor and MTBE as the hydrogen bond acceptor. The objective of this study is to estimate the strength of the hydrogen bond between MTBE and water, and to determine the structure of the MTBE-water clusters by means of high-level ab initio quantum mechanical and density functional theory calculations. The geometrical structures, vibrational frequencies, and stabilization energies of the MTBE-water complexes are fully corrected for basis set superposition error (BSSE).

Bailey, G.W., and Sawunyama, P. Biosurfaces and bioavailability: a nanoscale overview. Presented at: Bouyoucos Conference on Molecular Level Processes Controlling Availability of Chemical Species to Plants and Animals, Chalkidiki, Greece, June 23-28, 2002.

6/23/2002

**Contact:** George W. Bailey

**Abstract:** Environmentally, contaminant bioavailability is a key parameter in determining exposure assessment and ultimately risk assessment/risk management. Defining bioavailability requires knowledge of the contaminant spatial/temporal disposition and transportability and the thermodynamic activity of the contaminant in the system. Different chemical species of the same substance will vary in their biological availability and toxicity, and this availability and toxicity will change depending on the type of organism being considered (i.e., whether it is humans, other animals or plants). The interplay of various biogeochemical processes -- adsorption/ desorption, complexation precipitation/dissolution (including biomineralization), speciation, abiotic and biotic transformation ? defines contaminant bioavailability/activity. At the center of the biogeochemical processes are environmental surfaces. Environmental surfaces (mineral, organic, biological, and composite) determine the physicochemical and biological properties of soils and control the chemical reactivity, fate, transport, transformation and bioavailability of nutrients and chemical contaminants in soil ecosystems. In this presentation we will examine the nature and character of biosurfaces --lignin, humics, polysaccharides, proteins, and cell walls of bacteria, fungi and algae. This will be done by scrutinizing the structure, morphology, chemical composition, chemical functionality, electronic properties, and hydrophobic/hydrophilic character of each biosurface type. Such scrutiny will be done through the "eyes" of scanning probe microscopy, spectroscopy, computational chemistry and virtual reality. Interpretation of such an examination will be couched in terms of a 3-dimensional, holistic, and dynamic perception of soil.

Sawunyama, P., and Bailey, G.W. Methyl tert-butylether-water interaction. Presented at: American Society of Agronomy-Crop Science Society of America-Soil Science Society of America Annual Meeting, Indianapolis, IN, November 10-14, 2002.

11/11/2002

**Contact:** George W. Bailey

**Abstract:** Methyl tert-butyl ether (MTBE) is a well-known environmental contaminant owing to its high solubility in water. Since the early 1990s, MTBE has been added to gasoline to improve air quality in some metropolitan areas of the United States. Improved air quality was, however, achieved at the expense of MTBE tainted water. MTBE from leaking underground gasoline tanks, urban runoff, boats, etc., has been contaminating surface water and ground water in the very areas MTBE use was supposed to improve air quality. Molecular association between MTBE and water is predominantly via hydrogen bonding with water acting as the hydrogen bond donor and MTBE as the hydrogen bond acceptor. The objective of this study is to estimate the strength of the hydrogen bond between MTBE and water, and to determine the structure of the MTBE-water clusters by means of high-level ab initio quantum mechanical and density functional theory calculations. The geometrical structures, vibrational frequencies, and stabilization energies of the MTBE-water complexes are fully corrected for basis set superposition error (BSSE).

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Richardson, S.D. Career opportunities at the U.S. EPA. Presented at: 223rd American Chemical Society National Meeting, Orlando, FL, April 7-11, 2002.

4/7/2002

**Contact:** Susan D. Richardson

**Abstract:** Careers in the government-environmental sector can be extremely rewarding, as much of what you do can have a direct impact. For example, I have worked for 12 years at the U.S. EPA's National Exposure Research Laboratory, and have focused on identifying chemical disinfection by-products (DBPs) in drinking water. Once the DBPs are identified, health effects research is conducted to determine whether any pose a hazard to human health. Results of this research are used to minimize those DBPs that pose a risk to human health and to ultimately improve the safety of our drinking water. So, in addition to having opportunities to publish research, EPA researchers have the additional opportunity to have a direct impact both in human health issues and in ecological issues. Other government agencies, such as the U.S. Geological Survey offer similar opportunities. There are also non-research career opportunities for chemist in EPA and in other government agencies. Research and non-research career opportunities will be discussed.

Richardson, S.D., Thruston, Jr., A.D., Krasner, S.W., and Weinberg, H.S. Results of the nationwide DBP occurrence study: identification of new and interesting DBPs. Presented at: International Society of Exposure Analysis - International Society of Environmental Epidemiology Conference, Vancouver, Canada, August 11-15, 2002.

8/11/2002

**Contact:** Susan D. Richardson

**Abstract:** Drinking water disinfection by-products (DBPs) are formed when disinfectants, such as chlorine, react with natural organic matter and bromide present in the water. Chloroform was the first DBP identified in drinking water (in 1974), and was subsequently shown (along with other trihalomethanes, bromodichloromethane, dibromochloromethane, and bromoform) to cause cancer in laboratory animals. In the 25 years following the discovery of chloroform, several hundred DBPs have been identified and reported in the literature. However, only a very few DBPs have been studied for adverse health effects. Because health effects studies are extremely expensive (\$1-2 million), it is not possible to simply test all DBPs that are reported. Also, it is not wise to test DBPs for which there is no quantitative occurrence information (to know how widespread a particular DBP was and at what concentrations it is present). Therefore, we have initiated a nationwide occurrence study to quantify 'high priority' DBPs and to identify any new ones that have not been previously reported. The DBPs to be quantified were the result of a major effort by experts who scrutinized all DBPs reported in the literature for probable adverse health effects (based on their chemical structures). The 'top 50' DBPs resulting from this prioritization were included for this nationwide occurrence study. Drinking water samples are being collected across the U.S. from waters that use chlorine, ozone, chlorine dioxide, or chloramine for disinfection. Results from the quantitation of the approximately 50 high priority DBPs will be presented in an accompanying paper by Krasner et al. This paper will detail the identification of new, previously unidentified DBPs in the drinking water samples. These DBPs include many new brominated DBPs including bromo-acids (such as dibromopropenoic acid, tribromopropenoic acid, and dibromobutanoic acid), bromo-ketones, and bromo-acetaldehydes, such as dibromoacetaldehyde.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Richardson, S.D., Thruston, Jr., A.D., McKague, B., Rav-Acha, C., and Glezer, V. Identification of new brominated acids in drinking water. Presented at: 50th American Society for Mass Spectrometry Conference, Orlando, FL, June 2-6, 2002.

6/2/2002

**Contact:** Susan D. Richardson

**Abstract:** Since chloroform was identified as the first disinfection by-product (DBP) in drinking water, there has been more than 25 years of research on DBPs. Despite these efforts, more than 50% of the total organic halide (TOX) formed in chlorinated drinking water remains unknown. There is even less known about the identity of DBPs formed by alternative disinfectants, such as ozone, chlorine dioxide, and chloramine. The understanding of DBPs is important because epidemiologic studies have indicated a potential risk of cancer and reproductive/developmental effects resulting from the consumption of disinfected tap water. Recent epidemiologic and toxicologic studies have also indicated that the bromine-containing DBPs may be more toxicologically important than the chlorinated analogs. In this study, we report the identification of new, potentially toxicologically significant, brominated acids that were not previously known. These new brominated acids were identified using GC/MS. High resolution electron ionization mass spectrometry was used to confirm potential empirical formulas suggested through the interpretation of the mass spectra. Drinking water samples were treated with pre-chlorination followed by chlorine dioxide-chloramine treatment, and were collected from a major drinking water treatment plant in Israel, whose source water contains extremely high levels of bromide. It is the presence of this natural bromide that allows the formation of bromine-containing DBPs. Drinking water samples were acidified and extracted with XAD resins (8 over 2). The resins were eluted with ethyl acetate, and the resulting extracts were rotoevaporated to 1 mL and methylated using BF<sub>3</sub>/methanol. The bromine-containing acids were identified as the derivatized methyl esters. A few of these compounds were present in the spectral library databases (NIST and Wiley), but many were not. Therefore, fragmentation patterns in their mass spectra had to be interpreted and tentative identifications assigned. High resolution MS was used to confirm empirical formula assignments for the molecular ions and the fragments. In addition to the commonly observed brominated acetic acids, interesting new bromo-acids were identified, including brominated propanoic acids, propenoic acids, butanoic acids, butenoic acids, and dioic acids. The following compounds were confirmed through the analysis of standards (most of which were prepared synthetically): 2-bromobutanoic acid; 4-bromobutanoic acid; 3,3-dibromopropenoic acid; 2,3-dibromopropenoic acid; 2,3-dibromobutenoic acid, tribromopropenoic acid; threo-2,3-dibromobutanedioic acid; and trans-dibromobutanedioic acid.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Vincenti, M., Davit, P., and Richardson, S.D. Comparison of perfluorinated chloroformates as direct aqueous sample derivatizing agents for highly hydrophilic analytes. Presented at: 50th American Society for Mass Spectrometry Conference, Orlando, FL, June 2-6, 2002.

6/2/2002

**Contact:** Susan D. Richardson

**Abstract:** Strong oxidants are supposed to produce quite extensive cleavage of the hydrocarbon backbone of natural organic matter, resulting in the release of partly oxidized organic molecules. The identification and detection of these small and highly polar compounds represents a challenging task, since they cannot be extracted from the aqueous matrix or concentrated. Moreover, their direct instrumental detection in the original matrix is difficult due to inadequate sensitivity, lack of chromophores for spectroscopic detection, and low and noisy molecular ion signal for mass spectrometric detection. Typical analytes of this kind are polycarboxylic acids, hydroxyacids, ketoacids, glyoxals, hydroxylamines, aminoacids, aminoalcohols, and glycols. Direct aqueous sample derivatization is a promising approach to convert the analyte polar functional groups into more hydrophobic ones, allowing their extraction. However, most derivatizing agents are instantly hydrolyzed as they interact with water-containing solvents. We have developed a series of derivatization procedures based on hydrophobic chloroformates, which operate preferentially in purely aqueous solutions, while the addition of any organic solvent disfavors, instead of favoring, the derivatization yields. The commercially available prototype of these hydrophobic reagents is n-hexyl chloroformate. We have recently synthesized a series of perfluoroalkyl and perfluoroaryl chloroformates, in order to produce more volatile derivatives and to achieve high sensitivity and selectivity by electron capture negative ionization MS detection. The series of perfluorinated chloroformates that we have synthesized includes 2,2,3,3,4,4,5,5-octafluoropentyl, 2-chloro-2,2,3,3,4,4,5,5-octafluoropentyl, 3,3,4,4,5,5,6,6,7,7,8,8,8-tridecafluorooctyl, pentafluorobenzyl, and 2-(pentafluorophenoxy)ethyl chloroformates. Upon derivatization, carboxylic acids, alcohols, and amines are converted into esters, carbonates, and carbamates, respectively, which have no more hydrophilic character. When multiple functional groups are present in a single analyte structure, each one undergoes derivatization. The applicability and analytical performance of these five chloroformates for the derivatization of polar analytes in the aqueous-phase was compared, revealing interesting differences and preferences. The large number of fluorine atoms in the derivative structures confers high electron affinity to them, allowing extremely sensitive detection by ECNI-MS. Unfortunately, the ECNI mass spectra of the derivatives exhibit extensive fragmentation, which often prevents the detection of the molecular ion. On the other hand, positive ion CI spectra are more likely to provide the molecular ion information, but the detection limits in the positive ion mode is 3 orders-of-magnitude higher than in the negative ion mode. In the negative ion mode, the detection limits for most standard analytes are located in the low ppt range, as referred to the original concentration in water. Calibration curves are linear in a two

Viana, L., Pinto, A., Bustamante, M., Molina, M., Zepp, R.G., and Kisselle, K. Structure of microbial communities in native and converted savanna areas of central Brazil. Presented at: American Society for Microbiology Annual Meeting, Salt Lake City, UT, May 19-23, 2002.

5/19/2002

**Contact:** Marirosa Molina

**Abstract:** Brazilian savannas (Cerrado) have suffered drastic changes in land use with major conversion of native areas to agriculture since 1960. Burning, both due to natural conditions and as a human-induced practice, is a common event during the dry season (April to September) and plays a significant role in the conversion of areas. Although microorganisms have an important role in nutrient cycling and ecosystem functioning, the effect of land-use changes on microbial community structure and function is not well understood. We studied the effect of vegetation changes and fire regimes on the structure and dynamic of soil microbial communities using phospholipid fatty acid (PLFA) analysis. Soil samples (0-5cm) were collected from June/00 to June/01 in two native areas subjected to different fire regimes (2 plots protected from fire since 1992 and 2 plots submitted to prescribed fires) and in an old, active pasture (Brachiaria brizantha). Total PLFA ranged from 0.21 to 27.82 ug/g wet weight with the lower values determined during the dry season. Principal component analysis (PCA) separated microbial communities by vegetation type (native vs. pasture) and seasonality (wet vs. dry), explaining 34% and 13%, respectively, of the total PLFA variability. No significant difference was observed in the communities extracted from the two native areas regardless of the difference in vegetation cover or between the burned and unburned plots. Gram negative bacteria (16:1w7c, 16:1w5, 18:1w7c) were in higher concentrations in the pasture than in native areas, which were dominated by lipids with an eukaryotic origin and a type of Gram positive bacteria. Cy19:0 and 10Me16:0 explained most of the variability during the dry season while eukaryotic lipids explained most of the variability during the wet season. The data indicate a strong effect due to land conversion and no effect due to burning regimes in the structure of soil microbial communities.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Molina, M., and Burke, Jr., R.A. 13C-depleted microbial lipids indicate seasonal methanotrophic activity in shallow estuarine sediments. Presented at: American Society of Limnology and Oceanography Conference, Victoria, Canada, June 10-14, 2002.

6/10/2002

**Contact:** Marirosa Molina

**Abstract:** Compound specific isotope analysis was combined with phospholipid fatty acid (PLFA) analysis to identify methanotrophic activity in members of the sedimentary microbial community in the Altamaha and Savannah River estuaries in Georgia. 13C-depleted PLFAs indicate methane utilization because methane is the only C source with a depleted isotopic signal (-45 to -72 per mil) in these ecosystems. Three PLFAs (16:1w7, 16:1w5, and 10Me16:0) had 13C-depleted values (-52.37 to -39.2 per mil) during winter and spring when the salinity was less than 5 ppt. No depleted signal was observed during summer when the salinity was higher (4 to 30 ppt). 10Me16:0, an indicator of sulfate reducing bacteria (SRB), showed 13C-depleted values only in the Altamaha, indicating a discrepancy in the activity of specific functional groups depending on location. Methane production was higher in the Altamaha River than in the Savannah and its production did not correlate with the detection of 13C-depleted PLFAs. Our results suggest that methane oxidation occurs on a seasonal basis in highly dynamic estuaries and is the result of more than one microbial functional group (methanotrophs and SRB) in shallow estuarine sediments.

Molina, M. Microbial community diversity and carbon utilization in estuarine ecosystems of Southeastern U.S.A.. Presented at: Invited Speaker, University of Puerto Rico, Humacao, Puerto Rico, September 21, 2002.

9/21/2002

**Contact:** Marirosa Molina

**Abstract:** Estuaries are very dynamic ecosystems with regard to the transport and transformation of organic matter. Detrital organic matter is abundant in most estuaries, however, the dynamics of detritus utilization is not well understood. Two questions that remain unanswered are the sources of the detrital material and how the detritus is utilized by the different consumer groups in both the water column and surface sediments. A combination of phospholipid fatty acid analysis (PLFA) and compound specific isotope analysis (CSIA) was used to provide information on the possible sources, distribution, and transformation of sedimentary organic matter in the Altamaha and Savannah River estuaries in GA. Total PLFA concentration, a measurement of microbial biomass and community structure, was similar in both rivers. The highest microbial biomass was observed in the mesohaline zone apparently in response to an input of labile organic matter at the mixing zone. Microbial community structure differed significantly both as a function of time and type of river. Selective utilization of C sources by specific microbial groups was demonstrated with CSIA. This analysis indicated that Gram positive bacteria degraded 13C-enriched material (marine C), whereas Gram negative bacteria assimilated higher concentrations of C3 material. In general, the results indicated that estuarine systems under the influence of large riverine inputs are subjected to seasonal regimes of microbial C cycling in response to changes in rain episodes and river discharge. However, the seasonal variability of the system was readily altered by anthropogenic alterations to river flow and other land use changes; which then produced a shift in the natural C cycling at the sediment-water interface of the estuarine continuum.

Sundberg, S.E., Fisher, J.W., Ellington, J.J., Evans, J.J., and Keys, D. A simple model for the uptake, translocation, and accumulation of perchlorate in tobacco plants. Presented at: Annual Meeting Southeastern Regional Chapter of the Society of Toxicology, Athens, GA, October 31-November 1, 2002.

10/31/2002

**Contact:** James J. Ellington

**Abstract:** A simple mathematical model is being developed to describe the uptake, translocation, and accumulation of perchlorate in tobacco plants. The model defines a plant as a set of compartments, consisting of mass balance differential equations and plant-specific physiological parameters. The tobacco plant was subdivided into four major compartments for the model: solution, roots, stems, and leaves. Transport of perchlorate from the hydroponics solution through the roots, stems, and leaves was modeled by mass flow with the transpiration stream. Growth dilution was described by incorporating measured tobacco growth curves. Data obtained from a 13-day hydroponics growth study was used to determine plant growth curves and xylem flow rates as a function of time. There was good agreement between model predictions and measured concentrations for the solution and leaves, while soil and root concentrations were slightly under-predicted. Data obtained from a separate study with a wider solution concentration range was used to validate predicted leaf concentrations. This model, once adequately validated, can be applied more generally to other plants and chemicals currently used for phytoremediation and ecological risk assessment.

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*Presented Published*

Sundberg, S.E., Ellington, J.J., Evans, J.J., and Fisher, J.W. Phytoremediation of perchlorate by tobacco plants. Presented at: Annual Meeting Southeastern Regional Chapter of the Society of Toxicology, Athens, GA, October 31-November 1, 2002.

10/31/2002

**Contact:** James J. Ellington

**Abstract:** Previous studies have shown that tobacco plants are tolerant of perchlorate and will accumulate perchlorate in the plant tissues. The objective of this research was to determine the effectiveness of tobacco plants in phytoremediation, a technology that employs plants to degrade, extract, contain, or immobilize contaminants from soil and water. A 13-day hydroponics growth study under typical greenhouse conditions was completed to study the uptake, translocation, and bioaccumulation of perchlorate in tobacco plants. Ion chromatography (IC) was used for the quantitative analysis of perchlorate in the roots, stems, and leaves of the plant, and in the hydroponics growth media. The depletion of perchlorate in the hydroponics nutrient solution and the accumulation of perchlorate in the plant parts were determined at two-day intervals. Mass balance results show that perchlorate was not appreciably degraded by tobacco plants. Perchlorate primarily accumulated in the leaves of tobacco plants grown in a hydroponics solution fortified with known amounts of perchlorate. Results show that tobacco plants are effective in the phytoremediation of perchlorate.

Collette, T.W., and Williams, T.L. Speciation of organics in water with Raman spectroscopy: utility of ionic strength variation. Presented at: Federation of Analytical Chemistry and Spectroscopy Societies Conference, Providence, RI, October 13-17, 2002.

10/13/2002

**Contact:** Timothy W. Collette

**Abstract:** We have developed and are applying an experimental and mathematical method for describing the micro-speciation of complex organic contaminants in aqueous media. For our case, micro-speciation can be defined as qualitative and quantitative identification of all discrete forms of a chemical that co-exist as partners in coupled equilibria. We believe that this information is required to provide an accurate description of the fate and effects of many organic contaminants, both in natural ecosystems and in living organisms. An important example of this phenomenon is the co-existence of a zwitterion form and a true neutral form for molecules such as amino acids, hydroxypyridines, and atrazines. Our experimental method has thus far been based on collecting Raman spectra as a function of temperature. The zwitterion/neutral concentration ratio changes as a function of temperature according to the van't Hoff equation and can be fully described, in the simplest cases, using nonlinear modeling of the experimental data. However, the approach is not without limitations and constraining assumptions. For example, the temperature range is limited to the liquid state of water. The change in concentration ratio over this temperature range may not be dramatic enough to model with certainty in some cases. Also, the results may be confounded if multiple conformers of a given ionization form are present. Furthermore, the convenience, speed, accuracy, and precision of temperature control are limited. We have explored several ways to improve this Raman-based method. For example, we have used a high pressure sample chamber to increase the upper temperature limit. Also, we have investigated other domains in which the zwitterion/neutral concentration ratio varies; perhaps the most promising is ionic strength. While the zwitterion/neutral concentration ratio does not change as a function of pH, it does vary in a definable way as a function of ionic strength. In this talk we will describe our efforts to improve speciation measurements, focusing on preliminary results with ionic strength variation. In addition to alleviating some of the problems with the temperature-variant approach, the ionic strength-variant approach may also yield some new information that is of considerable thermodynamic importance.



Jan 1, 2002 - Dec 31, 2002

*Presented Published*

O'Niell, W.L., Jones, W.J., Whittemore, A., and Avants, J. Enantioselective reductive transformation of chiral polychlorinated biphenyls in lake sediment microcosms. Presented at: Third International Conference on Remediation of Chlorinated and Recalcitrant Compounds, Monterey, CA, May 20-23, 2002.

5/20/2002

**Contact:** William J. Jones

**Abstract:** The transformation rates and enantiomeric ratios of two chiral polychlorinated biphenyls (PCBs), 2,2',3,4',5',6-hexachlorobiphenyl (2,2',3,4',5',6-HCB) and 2,2',3,3',4,4',5,6-octachlorobiphenyl (2,2',3,3',4,4',5,6-OCB), were determined in anaerobic lake sediment microcosms (25°C). Similar experiments were conducted using Arochlor 1260, a mixture of chiral and non-chiral PCB congeners. Experimental treatments consisted of live (natural) sediment slurries, live slurries dosed with an organic nutrient mixture, live slurries dosed with 2,5-dibromobiphenyl (2,5-DBB) (as a "primer" to stimulate dehalogenation activity), live slurries dosed with both the nutrient mixture and 2,5-DBB, and autoclaved controls. The concentrations of the PCBs in the experimental microcosms were periodically analyzed by high-resolution gas chromatography/electron capture detection (GC/ECD) during a one year period. Analyses were conducted using both standard capillary columns and enantioselective capillary columns, and data were modeled to determine transformation rates. Enantiomer concentrations in transformed and unaltered (control) microcosms were compared to one another to assess enantioselective transformation of the PCB congeners. Transformation was absent or insignificant in sediment microcosms dosed with Arochlor 1260 or 2,2',3,3',4,4',5,6-OCB, but transformation was observed in microcosms dosed with 2,2',3,4',5',6-HCB. Transformation was observed in the live slurry plus nutrients treatment (89% loss), live slurry treatment (80% loss), live slurry plus 2,5-DBB and nutrients (63% loss), and live slurry plus 2,5-DBB but without nutrients (11% loss). No significant transformation was observed in the autoclaved controls. The 2,2',3,4',5',6-HCB was para-transformed to 2,2',3,5',6-pentachlorobiphenyl (2,2',3,5',6-PeCB) without apparent enantioselective transformation and then meta-transformed enantioselectively to 2,2',5',6-tetrachlorobiphenyl. It is interesting to note that enantioselective transformation occurred for the chiral intermediate (2,2',3,4',6-PeCB) and not for the chiral parent compound (2,2',3,4',5',6-HCB).

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

O'Niell, W.L., Jones, W.J., Whittemore, A., and Avants, J. Determination of transformation rates of chiral pesticides and PCBs in soil and sediment microcosms. Presented at: 8th Federation of the European Chemical Societies Conference on Chemistry and the Environment: Chemistry for a Sustaining World, Athens, Greece, September 1-4, 2002.

9/1/2002

**Contact:** William J. Jones

**Abstract:** Risk Based Corrective Action (RBCA) has gained widespread acceptance as a favorable approach to remediating contaminated sites. The use of RBCA methods often requires computer-based modeling to assess the fate and transport of hazardous contaminants in subsurface environments, and accurate modeling results require input of realistic transformation rates of the contaminants of concern. Unfortunately, relatively few microbial transformation rate studies have been conducted using natural soils or sediments, and have instead focused more on degradation of contaminants by pure microbial cultures. The purpose of our research was to compare degradation rates of selected pesticides and PCBs under different natural environmental conditions where the indigenous microbial population controlled degradation. Chiral contaminants were examined in this study to gain a better understanding of enantioselective transformation reactions. The microbial transformation rates and enantiomeric ratios of several chiral pollutants were determined in laboratory microcosms (25°C). Over 3,000 aerobic and anaerobic microcosms were prepared using agricultural soils from three different locations. The soil slurries were separately dosed with the following chiral pesticides: o, p'-DDT, o, p'-methoxychlor, cis-chlordane, trans-chlordane, heptachlor, heptachlor epoxide, and  $\alpha$ -HCH. In addition, approximately 500 microcosms were prepared anaerobically with lake sediment and separately dosed with a polychlorinated biphenyl mixture (Arochlor 1260) and the chiral PCB congeners 2,2',3,4',5',6-hexachlorobiphenyl and 2,2',3,3',4,4',5,6-octachlorobiphenyl. In all studies, experimental treatments consisted of live (natural) slurries, live slurries dosed with an organic nutrient mixture, and autoclaved controls. The concentrations of the chiral pollutants in the experimental microcosms were analyzed over a 2 year period using enantioselective high-resolution GC/MS, and data were modeled to determine transformation rates. Enantiomer concentrations in transformed and unaltered (control) microcosms were compared to assess enantioselective transformation of the chiral chemicals. Appreciable losses of the parent compounds were observed in microcosms dosed with o, p'-DDT, o, p'-methoxychlor, trans-chlordane, heptachlor,  $\alpha$ -HCH, and 2,2',3,4',5',6-hexachlorobiphenyl (Tables 1 and 2, and Figure 1). The addition of an organic nutrient mixture to the microcosms generally decreased transformation rates, and transformation was greater in microcosms incubated under anaerobic conditions. Transformation was insignificant in cis-chlordane, heptachlor epoxide, Arochlor 1260, and 2,2',3,3',4,4',5,6-octachlorobiphenyl dosed microcosms for most experimental treatments. Although statistically significant enantioselective transformation was not observed in most of the samples following approximately 2 years of incubation, differences in enantiomeric ratios were observed in selected samples dosed with 2,2',3,4',5',6-hexachlorobiphenyl and o, p'-DDT. The primary benefit of this study to other researchers will be the determination of realistic degradation rates that can be used in the mathematical simulation of the fate and transport of these hazardous compounds. Overall, these results can be used to protect human health and the environment by improving decision making for remedial actions. Additional research of this type may be directed toward determining the degradation rates of model compounds that can then be used to determine realistic transformation rates of other compounds with similar chemical structures.

Pakdeesusuk, U., Lee, C.M., Freedman, D.L., Coates, J.T., Wong, C.S., Jones, W.J., and Garrison, A.W. Enantioselectivity in the biodegradation of PCB atropisomers. Presented at: 23rd Annual Society of Environmental Toxicology and Chemistry Meeting, Salt Lake City, UT, November 16-20, 2002.

11/16/2002

**Contact:** William J. Jones

**Abstract:** Microcosms inoculated with sediment from two locations in a contaminated reservoir, Lake Hartwell, SC, USA, degraded certain PCB atropisomers enantioselectively while other atropisomers were degraded in racemic proportions. The microcosms were spiked with either 234-236 PCB (PCB132) or 236-245 PCB (PCB149). After a lag period, the enantiomers of both atropisomers were degraded in equal proportions with no change in the enantiomeric fraction (EF). The first products of dechlorination of both atropisomers were also atropisomers and were degraded enantioselectively. For example, the EF of PCB91 (236-24 PCB), the first product observed during the dechlorination of PCB132, changed from 0.42 to 0.03 over 140 days of incubation. PCB95, the first product observed for the dechlorination of PCB149, also showed a change in EF during the incubation. Microcosms spiked with Aroclor 1254 showed similar behavior in that PCB91 and PCB95 were degraded enantioselectively but PCB149 and PCB136 (236-236 PCB) were not. In all cases, methane production was initiated at the same time that dechlorination of the PCBs began in the microcosms. The chlorination pattern appeared to affect whether the biotransformation was racemic. Results point to the use of chiral analysis in understanding biotransformation mechanisms for PCBs in anaerobic environments.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Frick, W.E., and Barber, M.C. Compressible flow, entrainment, and megaplume. Presented at: 2002 Ocean Sciences Meeting, Honolulu, HI, February 11-15, 2002.

2/11/2002

**Contact:** Walter E. Frick

**Abstract:** It is generally believed that low Mach number, i.e., low-velocity, flow may be assumed to be incompressible flow. Under steady-state conditions, an exact equation of continuity may then be used to show that such flow is non-divergent. However, a rigorous, compressible fluid-dynamical derivation proves that the acceleration of fluid in radial laminar motion between parallel disks is proportional to the divergence of the velocity, and, to the contrary, velocity would be constant in non-divergent flow. Briefly, for an ideal gas in steady-state, laminar, and frictionless flow, four equations may be derived to solve the system exactly for the four unknowns -- density, pressure, temperature, and velocity -- without assuming incompressibility or non-divergence. This work shows that this finding is true for water as well. It also exploits the new theory to show that turbulent boundary layers, including jets and plumes, must consist of low-density fluid that expresses some of the corresponding low pressure through the equation of state. In the final analysis, the divergence of the fluid is established to be one of the basic mechanisms that causes turbulent flows to mix with the ambient fluid. The relationship between acceleration and divergence helps explain the role of jets in mixing. Similarly, it helps to explain jet and plume entrainment, including the entrainment of ambient fluid into oceanic megaplumes of volcanic origin.

Frick, W.E., Baumgartner, D.J., Denton, D.L., and Roberts, P.J.W. New developments of Visual Plumes - evaluation of bacterial pollution. Presented at: 2nd International Conference on Marine Waste Water Discharges, Istanbul, Turkey, September 16-20, 2002.

9/16/2002

**Contact:** Walter E. Frick

**Abstract:** Virulent or innocuous, high bacteria concentrations can force health authorities to close beaches, to the regret of the public and the communities that depend on the tourist trade for their livelihood. But, with real-time identification and measurement still in the future, often, by the time the incident has occurred, the potential danger has passed and perfectly safe beaches go unenjoyed (as many tests are based on harmless indicator bacteria). Instead, if reliable predictive models could be developed to accurately predict surfzone bacterial concentrations, the number of beach closures might be reduced significantly. Monitoring would serve the role of assuring model efficacy. The U.S. EPA Visual Plumes model is used to demonstrate how such a modeling system may ultimately function. It is also used to identify potential engineering practices, such as port design, to achieve greater rise to optimize the antiseptic effect of sunlight; to minimize nearshore impacts. Areas for immediate model improvement are identified and related potential health issues, such as toxics, are discussed.

Frick, W.E. Low-velocity compressible flow theory. Presented at: Seminar at University of Hong Kong, Kowloon, Hong Kong, December 12, 2002.

12/12/2002

**Contact:** Walter E. Frick

**Abstract:** The widespread application of incompressible flow theory dominates low-velocity fluid dynamics, virtually preventing research into compressible low-velocity flow dynamics. Yet, compressible solutions to simple and well-defined flow problems and a series of contradictions in incompressible flow theoretical arguments suggest that incompressible flow theory is not inevitable, robust, or powerful. As examples, it can be shown that the "incompressible" Bernoulli equation can be derived from the more general Euler equation without assuming constant density. Analytical compressible-flow solutions of simple laminar radial flow shows that compressible isothermal and compressible adiabatic solutions, as well as the corresponding incompressible solution, converge on the same relationship in the limit as velocity approaches zero, proving that the incompressible flow solution is but a special case of the more general compressible flow solution. More radically, it can be shown that adiabatic flow, the flow most often approximated in nature, cannot be accelerated without compressibility, that the pressure gradient must be supported by a density gradient, and, consequently, even low-velocity laminar flow is significantly divergent and compressible. The comparison of the linearized equation of state for an ideal gas to Einstein's famous energy-mass relationship underscores the absurdity of the notion that small density fluctuations are unimportant in low-velocity flow. Contradictions aside, low-velocity compressible flow theory explains otherwise theoretically unexplainable phenomena. For example, many insect and bird species appear to use compressible flow effects to fly efficiently. The development or suppression of turbulence in flow into and out of constrictions can be understood by applying compressible flow theory. Some low velocity geophysical flows and wave phenomena depend on compressible effects. And, finally, the basic properties of turbulent boundary layers are better explained and understood using compressible flow theory, promising to help fluid dynamicists better understand and exploit fluid-solids interactions.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Frick, W.E. Visual plumes concepts to potentially adapt or adopt in modeling platforms such as VISJET. Presented at: Seminar at University of Hong Kong, Kowloon, Hong Kong, December 10, 2002.

12/10/2002

**Contact:** Walter E. Frick

**Abstract:** Windows-based programs share many familiar features and components. For example, file dialogue windows are familiar to most Windows-based personal computer users. Such program elements are desirable because the user is already familiar with how they function, obviating the need for extra training. However, other common program elements, while simple and familiar, can detract from the usefulness and ease of use of the program. For example, many programs make excessive use of edit boxes, components that can receive numeric data. Tables often are a better alternative to large numbers of edit boxes. But even tables can present impediments to the user, or enforce repetition that can be annoying. One innovation in Visual Plumes is sparse-array tables used for inputting diffuser and ambient data. The sparse-array tables are designed around the concept of inheritance. In the diffuser table, for example, the first row of the table must have entries in all required columns, but, in the second and subsequent rows (representing additional cases), only values in columns with new values are input. In the absence of a change, Visual Plumes is programmed to assume that the missing variable in question inherits the value of the preceding case. This property of the tables makes it easy to examine a table for content, as constant values need not be unnecessarily repeated, and consequently do not hide significant changes from sight. In the ambient table this principle is extended, allowing special interpolations and extrapolations of data. This seminar examines Visual Plumes innovations in this context. Other innovations are discussed as well, as are perceived deficiencies of implementation. Some comparisons to the VISJET model help illustrate and contrast model features.

Weaver, J.W., and Tebes-Stevens, C.L. Uncertainty in model predictions-plausible outcomes from estimates of input ranges. Presented at: Brownfields 2002, Charlotte, NC, November 13-15, 2002.

11/13/2002

**Contact:** James W. Weaver

**Abstract:** Models are commonly used to predict the future extent of contamination given estimates of hydraulic conductivity, porosity, hydraulic gradient, biodegradation rate, and other parameters. Often best estimates or averages of these are used as inputs to models, which then transform them into output concentrations. All properties of the subsurface are both uncertain, because of imperfect measurement methods, and subject to point-to-point variability, because of geologic heterogeneity. Where used as purely predictive tools (i.e., in the absence of model calibration to field data), uncertainty and variability lead to the need for assessment of the plausible range of model outcomes. For Brownfields sites, the need to provide rapid assessment of contamination may not allow extensive field and modeling studies, where calibration data sets would be obtained. In those and other cases there is a need for evaluation of model uncertainty given input variation. Our approach is to use various combinations of input parameters to determine the earliest and latest first arrivals, the lowest and highest peak concentration and the shortest and longest duration of contamination. Results of simulations show that even moderate ranges of input variation generate significant differences in model predictions. These differences are greater than obtained from simple one parameter at a time uncertainty analyses, because of combined influences of multiple parameters. For example, hydraulic conductivity, porosity and gradient together determine the seepage velocity, and variation of each of parameter needs to be considered in order to determine the extremes of velocity. The extreme parameter sets were found to be different for each of the three predicted model outputs (first arrival, maximum concentration, duration). This result shows that selection of an average or worst case parameter set depends on the desired output of the model in ways that might not be guessed without performing an uncertainty analysis.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Weaver, J.W., Boufadel, M.C., and Naba, B. Transport studies in the Lock Lake tidal marsh of southern Long Island. Presented at: 2002 American Geophysical Union Spring Meeting, Washington, DC, May 28-31, 2002.

5/28/2002

**Contact:** James W. Weaver

**Abstract:** Ground water discharges directly into the Great South Bay and also via a sideways route into the Lock Lake tidal marsh at East Patchogue, New York. Data collected from the site were used to assess the transport of ground water contaminants into the waters of the Bay and potential ecological impacts on the marsh. Sampling included testing for evidence of salt water intrusion from the marsh, continuous water level recording in the aquifer and in marsh stilling wells, and salinity surveys at various locations in the marsh. The aquifer showed no evidence of salt water intrusion from the marsh, but the wells located up to 100 meters from the marsh were strongly influenced by tidal fluctuation. In these wells the direction of ground water flow varied by about 100° over one tidal cycle. Salinity measured at the single outlet of the marsh showed a consistent pattern of high salinity in outflow for about 3 hours after high tide. This was followed by declining salinity that was attributed to the outflow of Bay water recently mixed with fresh water inflows. A vertically-averaged model of the marsh was developed to simulate tidally-varying flows in the marsh, the average salinity in the marsh water, and transport of contaminants within the marsh. Model results show that the flow system is driven by gravity and bottom friction and that the bottom topography is critical for determining the character of flow.

Kraemer, S.R. Subsurface residence times as an algorithm for aquifer sensitivity mapping: testing the concept with analytic element ground water models in the Contentnea Creek basin, North Carolina, USA. Presented at: 2002 American Geophysical Union Spring Meeting, Washington, DC, May 28-31, 2002.

5/28/2002

**Contact:** Stephen R. Kraemer

**Abstract:** The objective of this research is to test the utility of simple functions of spatially integrated and temporally averaged ground water residence times in shallow "groundwatersheds" with field observations and more detailed computer simulations. The residence time of water in the subsurface is arguably a surrogate of aquifer sensitivity to contamination --- short contact time in subsurface media may result in reduced contaminant assimilation prior to discharge to a well or stream. Residence time is an established criterion for the delineation of wellhead protection areas. The residence time of water may also have application in assessing the connection between landscape and fair weather loadings of non-point source pollution to streams, such as the drainage of nitrogen-nitrate from agricultural fields as base flow. The field setting of this study includes a hierarchy of catchments in the Contentnea Creek basin (2600 km<sup>2</sup>) of North Carolina, USA, centered on the intensive coastal plain field study site at Lizzie, NC (1.2+km<sup>2</sup>), run by the USGS and the NC Dept. of Env. and Nat. Res. of Raleigh, NC. Analytic element models are used to define the advective flow field and regional boundary conditions. The issues of conceptual model complexity are explored using the multi-layer object oriented analytic element model Tim, and by embedding the finite difference model MODFLOW within the analytic element model GFLOW (tm). The models are compared to observations of hydraulic head, base flow separations, and aquifer geochemistry and age dating evidence. The resulting insights are captured and mapped across the basin as zones of average aquifer residence time using the ArcView (tm) GIS tools. Preliminary results and conclusions will be presented.

Kraemer, S.R. Analytic element modeling for source water assessments of public water supply wells: case studies in glacial outwash and basin-and-range. Presented at: Geological Society of America Annual Meeting, Denver, CO, October 27-30, 2002.

10/28/2002

**Contact:** Stephen R. Kraemer

**Abstract:** Over the last 10 years the EPA has invested in analytic elements as a computational method used in public domain software supporting capture zone delineation for source water assessments and wellhead protection. The current release is called WhAEM2000 (wellhead analytic element model). The program provides an interactive computer environment for design of protection areas based on radius methods, well in uniform flow solutions, and geohydrologic modeling. Protection areas are interactively designed and using electronic maps based on the US Geological Survey Digital Line Graph (DLG). Geohydrologic modeling for steady pumping wells, including the influence of hydrological boundaries, such as rivers, recharge, no-flow boundaries, and inhomogeneity zones, is accomplished using the analytic element method. Reverse gradient tracelines emanating from the pumping center of known residence time are used to delineate the capture zones. Two case studies will be presented: the Vincennes, IN wellfield located in glacial outwash; and the Salt Lake City, UT wellfield located in the basin and range.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Hayter, E.J. Modeling framework for evaluating sedimentation in stream networks: for use in sediment TMDL analysis. Presented at: National TMDL Science and Policy Conference, Phoenix, AZ, November 13-16, 2002.

11/13/2002

**Contact:** Earl J. Hayter

**Abstract:** A modeling framework that can be used to evaluate sedimentation in stream networks is described. This methodology can be used to determine sediment Total Maximum Daily Loads (TMDLs) in sediment impaired waters, and provide the necessary hydrodynamic and sediment-related data to a fish population model. Specifically, it can be used to calculate the maximum allowable load of sediment that can be carried to the streams from the surrounding watershed without exceeding the water quality target for the modeled streams. Watershed sediment loads are represented as nonpoint source loadings, and are calculated in units of tons of sediment per acre per year. The framework also accounts for instream sediment processes such as bank erosion and aggregation and degradation of the sediment beds in the modeled stream network. An application of the modeling framework to a reach of the Housatonic River in Massachusetts is described. The framework consists of coupled models that simulate both watershed and instream physical processes. The watershed portion of the framework consists of the U.S. EPA's Total Maximum Daily Load (TMDL) Universal Soil Loss Equation (USLE) model, that is a Windows-based software application for estimating diffuse (i.e., nonpoint) sediment source loads within a watershed. Specifically, this TMDL USLE program is useful for estimating the expected relative magnitude of land surface sediment loadings from different land use types within a watershed. The strength of the methodology is in estimating sediment loadings generated by erosion on agricultural lands. However, the USLE has also been applied to rangeland, forest lands, landfills, construction sites, mining sites, reclaimed lands, military training lands, parks, and other land uses where mineral soil material is exposed to the erosive forces of raindrop impact and overland flow. The instream portion of the framework consists of a model that simulates the hydrodynamics and sediment transport in stream networks. EFDC1D, a one-dimensional (1D) version of the three-dimensional (3D) version EFDC, can simulate bi-directional unsteady flows and has the ability to accommodate unsteady inflows and outflows associated with upstream inflows, lateral inflows and withdrawals, groundwater-surface water interaction, evaporation and direct rainfall (Hamrick 2001). EFDC1D also includes representation of hydraulic structures such as dams and culverts. For sediment transport, the model includes settling, deposition and resuspension of multiple size classes of cohesive and noncohesive sediments. The sediment bed is represented by multiple layers of mixed sediment classes. A bed consolidation model is implemented to predict time variations of bed depth, void ratio, bulk density and shear strength. The sediment bed representation is dynamically coupled to the cross-sectional area representation to account for area changes due to deposition and resuspension.

Rashleigh, B. Projecting the response of fish population growth rate to sediment exposure. Presented at: Georgia American Fisheries Society Meeting, Augusta, GA, January 29-31, 2002.

1/29/2002

**Contact:** Brenda Rashleigh

**Abstract:** Sediment is one of the main stressors on stream fish populations in Georgia. Here, a quantitative approach relating sediment exposure to stream fish population dynamics is presented, where equations characterize sediment exposure to vital rates, then vital rates are used in a matrix model to project dynamics. This analysis demonstrates how the approach can be used in TMDL development and identifies research needs to reduce uncertainty.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Rashleigh, B. Ecological endpoint modeling: effects of sediment on fish populations. Presented at: National Total Maximum Daily Loads Science and Policy Conference, Phoenix, AZ, November 13-16, 2002.

11/13/2002

**Contact:** Brenda Rashleigh

**Abstract:** Sediment is one of the main stressors of concern for TMDLs (Total Maximum Daily Loads) for streams, and often it is a concern because of its impact on biological endpoints. The National Research Council (NRC) has recommended that the EPA promote the development of models that can more effectively link environmental stressors (and control actions) to biological responses to support development of TMDLs. A quantitative approach relating sediment exposure to stream fish population dynamics is presented. An example is presented for a lithophilic, benthic insectivore fish species, such as a darter species, which is likely to be most sensitive to sediment impacts. First, equations are developed to characterize sediment exposure to the vital rates. Equations represent: the effects of suspended sediment and deposited sediment on feeding and food availability, and therefore survival; and the effect of deposited sediment on fecundity. Next, the vital rates are used in an age-structured population matrix model. A simple approach, a Leslie matrix, is presented. The matrix is used to examine the long-term population growth rate, which is given by the largest eigenvalue. A more realistic approach is an age-structured matrix that includes density-dependence. This type of matrix model is solved to give an equilibrium condition. Both the Leslie and density-dependent matrices are examined under the conditions of environmental stochasticity. These models can also be used to examine short-term population dynamics and to calculate sensitivity to different vital rates. The quantitative approach presented here can be used in TMDL development. A load allocation may be set based on the criterion that either the long term growth-rate is positive, or the equilibrium population size is above some minimum viable level. Results from the analysis of environmental stochasticity can be used to suggest a margin of safety for a TMDL. The use of models to simulate the response of ecological endpoints to sediment loading can lead to additional and improved management approaches for impaired streams.

Rashleigh, B., and Randall, D.J. Modeling the response of fish populations to eutrophication. Presented at: North Atlantic Treaty Organization/Committee on the Challenges of Modern Society Workshop, Ljubljana, Slovenia, May 6-12, 2002.

5/6/2002

**Contact:** Brenda Rashleigh

**Abstract:** Eutrophication resulting from nonpoint source pollution is one of the largest environmental problems in lakes and reservoirs around the world. Two characteristics of eutrophication, decreased dissolved oxygen and increased concentration of ammonia, are known to affect fishes. We developed a model to quantify population-level effects of eutrophication on fish. The model uses oxygen, ammonia, pH, and temperature outputs from water quality modeling studies as driving variables and incorporates results from individual-level fish toxicology studies of growth, survival, and reproduction conducted in the laboratory. The model is applied to Lake Peipsi in Estonia/Russia. We focus on two common, commercially-important fish species, smelt (prey) and pikeperch (predator). Preliminary results indicate that the two fish species respond similarly to eutrophication, the fish populations are most sensitive to changes in oxygen, and over time, ammonia and oxygen changes are synergistic in their effects on populations. Future issues include availability and quality of data for calibration, and the role of spatial variability of water quality conditions in the lake.

Cyterski, M.J., and Ney, J. Trophic dynamics of striped bass in Smith Mountain Lake, Virginia. Presented at: American Fisheries Society Annual Meeting, Baltimore, MD, August 18-22, 2002.

8/18/2002

**Contact:** Michael J. Cyterski

**Abstract:** We examined the adequacy of the forage base to meet demand of striped bass in Smith Mountain Lake, Virginia. In regards to prey supply, mean alewife biomass from 1993-1998 was 37 kg/ha and mean gizzard shad biomass from 1990-1997 was 112 kg/ha. Mean annual alewife surplus production was 73 kg/ha and mean annual gizzard shad surplus production totaled 146 kg/ha. Bioenergetics modeling coupled with population density estimates showed that striped bass consumed 46 kg/ha of alewife and 27 kg/ha of gizzard shad annually. The cumulative effect of morphology, behavior, and distribution on prey availability, in addition to consumption by other predators, was also quantified. For striped bass, available supply of gizzard shad surpassed demand by 30% but available alewife supply was only 4% greater than demand. Striped bass stockings were increased by 50% in 1998 and have remained at that level. A model that simulated the relationship between alewife abundance and mortality and the mortality, abundance, and growth of striped bass examined the consequences of increased striped bass stocking. Model output showed that a stocking increase had a near-zero probability of increasing the mean density of legal and citation striped bass in this system.



Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Babendreier, J.E., and Castleton, K.J. Investigating uncertainty and sensitivity in integrated multimedia environmental models: tools for 3MRA. Presented at: International Environmental Modelling and Software Society 2002 Biennial Meeting, Lugano, Switzerland, June 24-27, 2002.

6/25/2002

**Contact:** Justin E. Babendreier

**Abstract:** Sufficiently elucidating uncertainty and sensitivity structures in environmental models can be a difficult task, even for low-order, single-media constructs driven by a unique set of site-specific data. The ensuing challenge of examining ever more complex, integrated, higher-order models is a formidable one, particularly in regulatory settings applied on national scales that must ensure the continued protection of humans and ecology while preserving the economic viability of industry. Quantitative assessment of integrated, multi-media models that simulate hundreds of sites, spanning multiple geographical and ecological regions, will ultimately require a systematic, comparative approach coupled with sufficient computational power. The Multi-media, Multi-pathway, and Multi-receptor Risk Assessment Model (3MRA) is an important code, being developed by the United States Environmental Protection Agency, for use in risk assessment of hazardous waste management facilities. The model currently entails over 700 variables, 200 of which are explicitly stochastic. 3MRA starts with a chemical concentration in a waste management unit (landfill, waste pile, aerated tank, surface impoundment, or land application unit), estimates the release and transport of the chemical throughout the environment, and predicts associated exposure and risk. 3MRA simulates multi-media (air, water, soil, sediments), fate and transport, multi-pathway exposure routes (food ingestion, water ingestion, soil ingestion, air inhalation, etc.), multi-receptor exposures (resident, gardener, farmer, fisher, ecological habitats and populations; all with various cohort considerations), and resulting risk (human cancer and non-cancer effects, ecological population and community effects). 3MRA collates the output for an overall national risk assessment, offering a probabilistic strategy as a basis for regulatory decisions. Design of SuperMUSE, a 125 GHz PC-based, Windows-based supercomputer for Model Uncertainty and Sensitivity Evaluation is described, along with conceptual layout of an accompanying java-based parallelization software toolset. Initial sensitivity and uncertainty analyses of 3MRA are also presented with plans for conducting additional screening level and global sensitivity analysis techniques.

Babendreier, J.E. The relative importance of the vadose zone in multimedia risk assessment modeling applied at a national scale: an analysis of benzene using 3MRA. Presented at: 2002 American Geophysical Union Spring Meeting, Washington, DC, May 28-31, 2002.

5/28/2002

**Contact:** Justin E. Babendreier

**Abstract:** Evaluating uncertainty and parameter sensitivity in environmental models can be a difficult task, even for low-order, single-media constructs driven by a unique set of site-specific data. The challenge of examining ever more complex, integrated, higher-order models is a formidable one, particularly in regulatory settings applied on a national scale. Quantitative assessment of uncertainty and sensitivity within integrated, multimedia models that simulate hundreds of sites, spanning multiple geographical and ecological regions, will ultimately require a systematic, comparative approach coupled with sufficient computational power. The Multimedia, Multipathway, and Multireceptor Risk Assessment Model (3MRA) is an important code being developed by the United States Environmental Protection Agency for use in site-scale risk assessment (e.g. hazardous waste management facilities). The model currently entails over 700 variables, 185 of which are explicitly stochastic. The 3MRA can start with a chemical concentration in a waste management unit (WMU). It estimates the release and transport of the chemical throughout the environment, and predicts associated exposure and risk. The 3MRA simulates multimedia (air, water, soil, sediments), pollutant fate and transport, multipathway exposure routes (food ingestion, water ingestion, soil ingestion, air inhalation, etc.), multireceptor exposures (resident, gardener, farmer, fisher, ecological habitats and populations), and resulting risk (human cancer and non-cancer effects, ecological population and community effects). The 3MRA collates the output for an overall national risk assessment, offering a probabilistic strategy as a basis for regulatory decisions. To facilitate model execution of 3MRA for purposes of conducting uncertainty and sensitivity analysis, a PC-based supercomputer cluster was constructed. Design of SuperMUSE, a 125 GHz Windows-based Supercomputer for Model Uncertainty and Sensitivity Evaluation is described, along with the conceptual layout of an accompanying java-based paralleling software toolset. Preliminary work is also reported for a scenario involving Benzene disposal that describes the relative importance of the vadose zone in driving risk levels for ecological receptors and human health. Incorporating landfills, waste piles, aerated tanks, surface impoundments, and land application units, the site-based data used in the analysis included 201 national facilities representing 419 site-WMU combinations.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

**BOOK CHAPTER**

Loux, N.T. "Effective acidity-constant behavior near zero-charge conditions." In: Interfacial applications in environmental engineering, Chapter 11 Keane, M.A. (Ed.), New York, NY: Marcel Dekker, Inc. 2002, 193-214.

12/15/2002

**Contact:** Nicholas T. Loux

**Abstract:** Current geochemical paradigms for modeling the solid/water partitioning behavior of trace toxic ionic species at subsaturation mineral solubility porewater concentrations rely on two fundamental mechanisms: (1) solid solution formation with the major element solid phases present in the environment, and (2) adsorption reactions on environmental surfaces. Solid solution formation is the process leading to the substitution of a trace ion for a major ion in a natural solid phase. The second mechanism, the topic of this chapter, is generally believed to be more widespread in environmental systems and is frequently described as the result of surface complexation reactions between ionizable species ( $\text{Mez}^+$ ) and reactive surface sites (less than  $\text{SOH}$ ) present on environmental solids, including iron oxides, manganese oxides, aluminum oxides, silicon oxides, aluminosilicates, and particulate organic carbon.

Zepp, R.G. "Solar ultraviolet radiation and aquatic carbon, nitrogen, sulfur and metals cycles." In: UV Effects in Aquatic Organisms and Ecosystems, Chapter 5 E.W. Helbling and H. Zagarese (Ed.), Cambridge, UK: Royal Society of Chemistry 2002, 137-183. EPA/600/A-03/019.

11/1/2002

**Contact:** Richard G. Zepp

**Abstract:** Solar ultraviolet radiation (290-400 nm) has a wide-ranging impact on biological and chemical processes that affect the cycling of elements in aquatic environments. This chapter uses recent field and laboratory observations along with models to assess these impacts on carbon, nitrogen, sulfur and metals cycles. Much emphasis is placed on the interactions of LJV radiation with carbon capture and storage, decomposition, and trace gas exchange. UV exposure generally inhibits phytoplankton photosynthesis and also affects microbial processes both through direct inhibition of bacterial activity as well as through effects on the biological availability of carbon and nitrogen substrates. One important aspect of LJV interactions with carbon cycling involves the formation and decomposition of UV-absorbing organic matter, principally chromophoric dissolved organic matter (CDOM). CDOM controls UV exposure in the sea in many freshwater environments and it can be directly photodecomposed to dissolved inorganic carbon, carbon monoxide, and various carbonyl-containing compounds. UV can potentially affect nitrogen and sulfur cycling in a variety of ways including alterations in nitrogen fixation, effects on the biological availability of dissolved organic nitrogen, UV photoinhibition of organisms such as bacterioplankton and zooplankton that affect sources and sinks of dimethylsulfide (DMS) and UV-initiated photoreactions that oxidize DMS and produce carbonyl sulfide. Metal cycling also interacts in many ways with UV radiation via photoinhibition of microbial redox cycling, direct photoreactions of dissolved metal complexes and of metal oxides and indirect reactions that are mediated by photochemically-produced reactive oxygen species (ROS). Photoreactions can affect the biological availability of essential trace nutrients such as iron and manganese, transforming the metals from complexes that are not readily assimilated to free metal ions or metal hydroxides that are available.

**JOURNAL**

Russo, R.C. Development of marine water quality criteria. Marine Pollution Bulletin 45 (1-12):84-91 (2002). EPA/600/J-03/075.

9/1/2002

**Contact:** Rosemarie C. Russo

**Abstract:** The U.S. Environmental Protectional Agency has developed guidelines for deriving numerical national water quality criteria for the protection of aquatic organisms and their uses. These guidelines provide the method for deriving water quality criteria, including minimum data base requirements, data evaluation procedures, and calculations. The guidelines have been in place for a long time, and states have used them to derive water quality standards for their waterbodies. More recent efforts have been directed towards the development of technical guidance based on the concept that bioassessment and biocriteria programs for estuaries and near coastal waters are interrelated and are critical components of comprehensive water resource protection and management. This is a holistic approach to protection and management, integrating biological assessments into traditional chemical and physical evaluations and augmenting the established water quality criteria. The method for deriving water quality criteria and the approach for biocriteria development for marine systems are described.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Teske, M.E., Bird, S.L., Esterly, D.M., Curbishley, T.B., Ray, S.L., and Perry, S.G. AgDRIFT: a model for estimating near-field spray drift from aerial applications. Environmental Toxicology and Chemistry 21 (3):659-671 (2002). EPA/600/J-02/139. 3/1/2002

**Contact:** Sandra L. Bird

**Abstract:** The aerial spray prediction model AgDRIFT(R) embodies the computational engine found in the near-wake Lagrangian model AGricultural DISPersal (AGDISP) but with several important features added that improve the speed and accuracy of its predictions. This article summarizes those changes, describes the overall analytical approach to the model, and details model implementation, application, limits, and computational utilities.

Bird, S.L., Perry, S.G., Ray, S.L., and Teske, M.E. Evaluation of the AgDISP aerial spray algorithms in the AgDRIFT model. Environmental Toxicology and Chemistry 21 (3):672-681 (2002). EPA/600/J-02/138. 3/1/2002

**Contact:** Sandra L. Bird

**Abstract:** A systematic evaluation of the AgDISP algorithms, which simulate off-site drift and deposition of aerially applied pesticides, contained in the AgDRIFT model was performed by comparing model simulations to field-trial data collected by the Spray Drift Task Force. Field-trial data used for model evaluation included 161 separate trials of typical agriculture aerial applications under a wide range of application and meteorological conditions. Input for model simulations included information on the aircraft and spray equipment, spray material, meteorology, and site geometry. The model input datasets were generated independently of the field deposition results, i.e., model inputs were in no way altered or selected to improve the fit of model output to field results. AgDRIFT shows a response similar to that of the field observations for many application variables (e.g., droplet size, application height, wind speed). However, AgDRIFT is sensitive to evaporative effects, and modeled deposition in the far-field responds to wet bulb depression whereas the field observations did not. The model tended to overpredict deposition rates relative to the field data for far-field distances, particularly under evaporative conditions. AgDRIFT was in good agreement with field results for estimating near-field buffer zones needed to manage human, crop, livestock, and ecological exposure.

Bird, S.L., Alberty, S.W., and Exum, L.R. Generating high quality impervious cover data. Quality Assurance 8 (2):91-103 (2000). EPA/600/J-02/133. 1/5/2002

**Contact:** Sandra L. Bird

**Abstract:** Nonpoint source pollution (NPS) from urban/ suburban areas is rapidly increasing as the population increases in the United States. Research in recent years has consistently shown a strong relationship between the percentage of impervious cover in a drainage basin and the health of the receiving stream. In this paper we quantify the amount of impervious cover within 56 14-digit hydrologic unit codes (HUCs) in Frederick County, Maryland, USA. This test data set will help in the development of regionwide impervious cover estimation methodologies. The software, sampling and analysis systems were developed to yield accurate and reproducible results. Digital orthophoto quarter quadrangles (DOQQ) from the U.S. Geological Survey were chosen as the basic media for the analysis. Ground features were identified and categorized by human analysts with the help of Geographic Information System (GIS) software and a prototype "cover tool" extension.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Bouchard, D.C. Cosolvent effects on sorption isotherm linearity. Journal of Contaminant Hydrology 56 (3-4):159-174 (2002). EPA/600/J-03/068.

6/1/2002

**Contact:** Dermont Bouchard

**Abstract:** Sorption-desorption hysteresis, slow desorption kinetics, and other nonideal phenomena have been attributed to the differing sorptive characteristics of the natural organic polymers associated with soils and sediments. In this study, aqueous and mixed solvent systems were used to investigate the effects of a cosolvent, methanol, on sorption isotherm linearity with natural organic matter (NOM), and to evaluate whether these results support, or weaken, the rubbery/glassy polymer conceptualization of NOM. All of the sorption isotherms displayed some nonlinear character. Our data indicates that all of the phenanthrene and atrazine isotherms were nonlinear up to the highest equilibrium solution concentration to solute solubility in water or cosolvent ratios (Ce/Sw,c) used, approximately 0.018 and 0.070, respectively. Isotherm linearity was also observed to increase with volumetric methanol content (fc). This observation is consistent with the NOM rubbery/glassy polymer conceptualization: the presence of methanol in NOM increased isotherm linearity as do solvents in synthetic polymers, and suggests that methanol is interacting with the NOM, enhancing its homogeneity as a sorptive phase so that sorption is less bimodal as fc increases. When the equilibrium solution concentration was normalized for solute solubility in water or methanol-water solutions, greater relative sorption magnitude was observed for the methanol-water treatments. This observation, in conjunction with the faster sorption kinetics observed in the methanol-water sediment column systems, indicates that the increase in relative sorption magnitude with fc may be attributed to the faster sorption kinetics in the methanol-water systems, and hence greater relative sorptive uptake for the rubbery polymer fraction of NOM at similar time scales.

Lewis, D.L., Gattie, D.K., Novak, M.E., Sanchez, S., and Phumphrey, C. Interactions of pathogens and irritant chemicals in land-applied sewage sludges (biosolids). BMC Public Health 2 (1):11 (2002). EPA/600/J-03/062, <http://www.biomedcentral.com/1471-2458/2/11>.

6/28/2002

**Contact:** David L. Lewis

**Abstract:** We report the results of a preliminary assessment of illnesses among 48 residents living near and downwind of nine land application sites. This assessment indicated that a pattern of chemical irritation developed from exposure to dusts and other airborne sludge contaminants followed by bacterial infections of the skin and respiratory tract. During the first month of exposure, approximately one-fourth of residents reporting chemical irritation experienced Staphylococcus aureus infections (furuncles, folliculitis, pneumonia, septicemia), an incidence 27 times that of a high-risk group (hospitalized patients). These results suggest that future research should address risks from exposure to airborne dusts and synergistic effects between irritant chemicals and low levels of pathogens, especially staphylococci.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Lewis, D.L., and Gattie, D.K. Pathogen risks from applying sewage sludge to land. Environmental Science & Technology 36 (13):286A-293A (2002). EPA/600/J-03/151.

7/1/2002

**Contact:** David L. Lewis

**Abstract:** Congress banned ocean dumping of municipal wastes in the late 1980s. In its place, EPA developed guidance (40 CFR Part 503) for land application of processed sewage sludge (biosolids), mainly for agricultural purposes (1). Public health and environmental concerns with processed sewage sludge have historically centered on heavy metals, pesticides, PCBs, and other chemical contaminants (2). The 503 rule, promulgated in 1993, included no formal risk assessment for bacteria, viruses, and other disease-causing microorganisms (3). Now, amid a growing number of complaints of illnesses and sporadic deaths among residents living near land application sites, a debate rages over whether risks ? especially from pathogens ? should have been more carefully assessed (see Figure 1). Illnesses reported by people exposed to dusts and water runoff from fields treated with sewage sludge indicate a pattern of chemical irritation ? burning eyes, burning lungs, difficulty in breathing, and skin rashes. These symptoms are followed within days to months with complaints of gastrointestinal, skin, and respiratory infections (4). Such reports are dismissed outright by proponents of land application practices as purely anecdotal. They argue that the only problem is public perception and point to a lack of documented cases of illnesses as proof that the practice is well managed and safe. Those impacted, however, argue that adverse effects are not monitored and proper epidemiological studies have never been done. Unfortunately, arguments on both sides are based on what science has not been done. It is not a dispute over interpretation of data, but over how to interpret the lack of data. Unlike other public health organizations grappling with threats of infectious diseases, EPA has relatively little expertise in infection control, no system or plan for monitoring infectious diseases nationwide, and provides virtually no resources to states to carry out its regulations in this area (5). Yet, the agency has the responsibility of overseeing the processing and disposal of, collectively, what is likely to be the nation's largest repository of infectious human material. On the other hand, unlike the federal Centers for Disease Control and Prevention (CDC), EPA is a regulatory agency. Its rules and regulations carry the force of law and violations are subject to criminal penalties. EPA is currently collaborating with the CDC to jointly assess potential land application problems. A properly managed national biosolids program that merges the expertise of the CDC with the regulatory authority of the EPA may be the best way to ensure that public health and the environment are adequately protected in this area.

Medina, V.F., Larson, S.L., and McCutcheon, S.C. Evaluation of continuous flow-through phytoreactors for the treatment of TNT-contaminated water. Environmental Progress 21 (1):29-36 (2002). EPA/600/J-03/071.

4/1/2002

**Contact:** Steven C. Mccutcheon

**Abstract:**

Susarla, S., Medina, V.F., and McCutcheon, S.C. Phytoremediation: An ecological solution to organic chemical contamination. Ecological Engineering 18 (5):647-658 (2002). EPA/600/J-03/073.

6/15/2002

**Contact:** Steven C. Mccutcheon

**Abstract:** Phytoremediation is a promising new technology that uses plants to degrade, assimilate, metabolize, or detoxify metals, hydrocarbons, pesticides, and chlorinated solvents. In this review, in situ, in vivo and in vitro methods of application are described for remediation of these compounds. Phytoaccumulation, phytoextraction, phytostabilization, phytotransformation, phytovolatilization and rhizodegradation are discussed and the role of enzymes in transforming organic chemicals in plants is presented. The advantages and constraints of phytoremediation are provided. Our conclusions is that phytoremediation prescriptions must be site-specific; however, these applications have the potential for providing the most cost-effective and resource-conservative approach for remediating sites contaminated with a variety of hazardous chemicals.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Colon, D., Weber, E.J., and Baughman, G.L. Sediment-associated reactions of aromatic amines. 2. QSAR development. Environmental Science & Technology 36 (11):2443-2450 (2002). EPA/600/J-03/072.

6/1/2002

**Contact:** Eric J. Weber

**Abstract:** The fate of aromatic amines in soils and sediments is dominated by irreversible binding through nucleophilic addition and oxidative radical coupling. Despite the common occurrence of the aromatic amine functional group in organic chemicals, the molecular properties useful for predicting reaction kinetics in natural systems have not been thoroughly investigated. Towards this goal, the sorption kinetics for a series of anilines with substituents in the ortho-, meta- or para-positions were measured in sediment slurries. The sorption kinetics of the substituted anilines were characterized by an initial, rapid sorption process followed by a much slower sorption process. The initial rates of sorption varied with the type and position of the substituent group. Rate constants for the initial sorption process were correlated with molecular descriptors including ionization constants (pKa's), Hammett s-constants, polarographic half-wave potentials (E1/2), one-electron oxidation potentials (E1), highest occupied molecular orbital (HOMO) energies (EHOMO), and ionization energies (EIE). Based on the strength of linear correlations and the availability of data, ionization constants and Hammett s-constants appear to be the most useful molecular descriptors for predicting reaction rates of substituted anilines in the sediment slurries. The slow rates of sorption were much less sensitive to substituents effects than the rate constants for the faster sorption process suggesting that the slower process was not controlled by the rate of electron transfer (i.e., nucleophilic addition or radical formation), but was limited by the availability of covalent binding sites.

Pinto, A., Bustamante, M., Viana, L., Varella, R., Zepp, R.G., Burke, Jr., R.A., Molina, M., and Kisselle, K. Soil emissions of N2O, NO and CO2 in Brazilian savannas: Effects of vegetation type, seasonality, and prescribed fires. Journal of Geophysical Research 107 (D20):8089-8089 (2002). EPA/600/J-03/330.

10/15/2002

**Contact:** Richard G. Zepp

**Abstract:** Using closed chamber techniques, soil fluxes of NO, N2O and CO2 were measured from September 1999 through October 2000 in savanna areas in central Brazil (Cerrado) subjected to prescribed fires. Our studies focused on two vegetation types, cerrado stricto sensu (20-50% canopy cover) and campo sujo (open, grass-dominated), which were either burned every 2 years or protected from fire. Soil moisture and vegetation type were more important in controlling NO and CO2 fluxes than fire regime. N2O flux, however, could not be detected in any of the vegetation-fire treatments. NO emissions increased slightly after burning (1.0 NO-N CM-2 h-1), but quickly returned to levels equal to or slightly lower than pre-fire fluxes. In comparison, NO emissions increased 100-fold (to 10.5 ng NO-N cm-2 h-1) during a water addition experiment in unburned campo sujo and to 1.0 ng NO-N cm-2 h-1 with the first rains in unburned cerrado and to 1.9 ng NO-N cm-2 h-1 in burned cerrado. Although NO flux did not correlate with N availability, low NO and N2O emissions, low nitrification rates, and the majority of inorganic N in the form of NH4+ all indicate a conservative N cycle in the Cerrado. CO2 fluxes increased significantly with the onset of rain and during a water addition experiment. The highest CO2 measured in wet season was 6.3 mol CO2 m-2 s-1 in burned campo sujo. During the dry season, there were no differences between burned and unburned treatments (average flux 1.6 - 2.3 mol CO2 m-2 S-1. Differences between fire treatments of cerrado and campo sujo fluxes are attributed to differences in relative litter production and root activity.

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*Presented Published*

Kisselle, K., Zepp, R.G., Burke, Jr., R.A., Opsahl, S.P., Pinto, A., Bustamante, M., Viana, L., and Varella, R. Seasonal soil fluxes of carbon monoxide in burned and unburned Brazilian savannas. *Journal of Geophysical Research* 107 (D20):8051-8051 (2002). EPA/600/J-03/329.

10/15/2002

**Contact:** Richard G. Zepp

**Abstract:** Soil-atmosphere fluxes of carbon monoxide (CO) were measured from September 1999 through November 2000 in savanna areas in central Brazil (Cerrado) under different fire regimes using transparent and opaque static chambers. Studies focused on two vegetation types, cerrado stricto sensu (20-50% canopy cover) and campo sujo (open, scrubland), which were either burned every 2 years or protected from fire (for 26 years). CO emissions in transparent chambers varied seasonally with highest fluxes during the late dry season (August-October) and lowest fluxes late in the wet season (February-April). Daytime fluxes in the transparent chambers were always higher than in the opaque chambers. Similarly, a diurnal study showed negative fluxes for all nighttime measurements and positive measurements for all daytime measurements. No significant differences were found between the daytime annual average fluxes from unburned cerrado and unburned campo sujo ( $160 \times 109$  molec.  $\text{cm}^{-2} \text{s}^{-1}$  and  $190 \times 109$  molec.  $\text{cm}^{-2} \text{s}^{-1}$ , respectively). Fire increased soil surface CO emissions significantly in the burned cerrado plot. Thirty days after the fire, daytime CO production was over 10 times higher than that of the unburned cerrado ( $812.8 \times 109$  molecules  $\text{cm}^{-2} \text{s}^{-1}$  vs.  $76.8 \times 109$  molecules  $\text{cm}^{-2} \text{s}^{-1}$ ). The increase in CO production occurred in both transparent and opaque chambers, suggesting the fire created photochemically- and thermally-reactive precursors. Removal of litter and standing dead plant material from plots in unburned campo sujo and a pasture was shown to dramatically decrease CO emissions. CO production in burned plots (using opaque chambers) was similar to previous measurements from Venezuelan and African savannas.

Miller, W.L., Moran, M.A., Sheldon, W., Zepp, R.G., and Opsahl, S.P. Determination of apparent quantum yield spectra for the formation of biologically labile photoproducts. *Limnology and Oceanography* 47 (2):343-352 (2002). EPA/600/J-02/137.

3/1/2002

**Contact:** Richard G. Zepp

**Abstract:** Quantum yield spectra for the photochemical formation of biologically labile photoproducts from dissolved organic matter (DOM) have not been available previously, although they would greatly facilitate attempts to model photoproduct formation rates across latitudinal, seasonal, and depth-related changes in spectral irradiance. Apparent quantum yield spectra were calculated for two coastal environments from the southeastern U.S. using post-irradiation bacterial respiration as a measure of total labile photoproduct formation and a cut-off filter method to model spectral dependence. As has been the case for previously studied classes of DOM photoproducts (i.e., dissolved inorganic carbon, CO, and  $\text{H}_2\text{O}_2$ ), UV-B irradiance was significantly more efficient at forming labile photoproducts (i.e., compounds readily assimilated by marine bacterioplankton) than UV-A and visible irradiance. Calculations of DOM photoproduct formation in southeastern U.S. coastal surface waters indicate a formation ratio for biologically labile photoproducts:CO of 13:1. The slope of a natural log plot of the apparent quantum yield spectrum obtained for biologically labile photoproducts was similar to that for CO ( $0.028 \text{ nm}^{-1}$  vs.  $0.034 \text{ nm}^{-1}$ ). Modeled kinetic rates therefore indicate that the production ratio of these photoproduct classes is approximately maintained despite variations in the solar spectrum that occur with depth in a water column or distance from shore. Application of the apparent quantum yield to coastal regions worldwide predicts an annual formation rate of biologically labile photoproducts in coastal waters of  $206 \times 10^{12} \text{ g C}$ .



Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Hu, C., Muller-Karger, F.E., and Zepp, R.G. Absorbance, absorption coefficient, and apparent quantum yield: a comment on ambiguity in the use of these optical concepts. *Limnology and Oceanography* 47 (4):1261-1267 (2002). EPA/600/J-03/152.

4/15/2002

**Contact:** Richard G. Zepp

**Abstract:** Several important optical terms such as "absorbance" and "absorption coefficient" are frequently used ambiguously in the current peer-reviewed literature. Since they are important terms that are required to derive other quantities such as the "apparent quantum yield" of photoproduction, ambiguity in the application of these concepts leads to results that are difficult or impossible to interpret correctly. Such ambiguity also hinders comparison of results between studies, and ultimately harms proper parameterization of numerical models of oceanic processes as well as refinement of remote sensing algorithms. We review these concepts and the implications of such ambiguities. A few simple recommendations that follow conventions developed by optical oceanographers are provided to authors dealing with these concepts. In particular, the symbol "a" is recommended for the absorption coefficient (in Napierian form, m<sup>-1</sup>), which is also preferred over absorbance (dimensionless) when data are presented; the symbol "a" is not recommended for absorbance; the symbol "A" should be used with caution because although it has been widely used for absorbance in photochemistry and photobiology, it has also been used for absorptance in physics and optical oceanography; the term "absorptivity" is not recommended due to conflicting definitions in the current literature; the "pathlength" value should always be given whenever absorbance data are presented; and "normalization" of photoproduction rates to absorbance or absorption coefficient should be performed only on optically thin samples unless the inner filter effects are accounted for and corrected.

Sawunyama, P., and Bailey, G.W. A computational chemistry study of the environmentally important acid-catalyzed hydrolysis of atrazine and related 2-chloro-s-triazines. *Pest Management Science* 58 (8):759-768 (2002). EPA/600/J-03/074.

6/15/2002

**Contact:** George W. Bailey

**Abstract:** Many chlorine-containing pesticides, for example 2-chloro-s-triazines, are of great concern both environmentally and toxicologically. As a result, ascertaining or predicting the fate and transport of these compounds in soils and water is of current interest. Transformation pathways for 2-chloro-s-triazines in the environment include dealkylation, dechlorination (hydrolysis), and ring cleavage. This study explored the feasibility of using computational chemistry, specifically the hybrid density functional theory method, B3LYP, to predict hydrolysis trends of atrazine (2-chloro-4-ethylamino-6-isopropylamino-s-triazine) and related 2-chloro-s-triazines to the corresponding 2-hydroxy-s-triazines. Gas-phase energetics are described on the basis of calculations performed at the B3LYP/6-311++G(d,p)//B3LYP/6-31G\* level of theory. Calculated free energies of hydrolysis ( $\Delta G_{298}$ ) are nearly the same for simazine (2-chloro-4,6-di(ethylamino)-s-triazine), atrazine, and propazine (2-chloro-4,6-di(isopropylamino)-s-triazine), indicating that hydrolysis is not significantly affected by the side chain amine-nitrogen alkyl substituents. Aqueous solvation effects were examined by means of Self-Consistent Reaction Field methods (SCRF). Molecular structures were optimized at the B3LYP/6-31G\* level using the Onsager model, and solvation energies were calculated at the B3LYP/6-311++G(d,p) level using the isodensity surface polarizable continuum model (IPCM). The extent of solvent stabilization was greater for ionic species than neutral species. Likewise, solvation reduced the hydrolysis barrier for protonated atrazine by 36.0 kJ mol<sup>-1</sup>.

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*Presented Published*

Simmons, J.E., Richardson, S.D., Speth, T.F., Miltner, R.J., Rice, G., Schenck, K.M., Hunter, E.S. III, and Teuschler, L.K. Development of a research strategy for integrated technology-based toxicological and chemical evaluation of complex mixtures of drinking water disinfection byproducts. Environmental Health Perspectives 110 (Supplement 6):1013-1024 (2002). EPA/600/J-03/066.

12/15/2002

**Contact:** Susan D. Richardson

**Abstract:** Chemical disinfection of water is a major public health triumph of the 20th century. Dramatic decreases in both morbidity and mortality of water-borne diseases are a direct result of water disinfection. With these important public health benefits comes low-level, chronic exposure to a very large number of disinfection byproducts (DBPs), chemicals that are formed as a result of reaction of the chemical disinfectant with naturally occurring inorganic and organic material in the source water. This paper provides an overview of joint research planning by scientists residing within the various organizations of the US. EPA's Office of Research and Development (ORD). The purpose is to address concerns related to potential health effects from exposure to DBPs that cannot be addressed directly from toxicological studies of individual DBPs or simple DBP mixtures. Two factors motivate the need for such an investigation of complex mixtures of DBPs: 1) a significant amount of the material that makes up the total organic halide and total organic carbon portions of the DBPs has not been identified; and 2) epidemiologic data, while not conclusive, are suggestive of potential developmental, reproductive or carcinogenic health effects in humans exposed to DBPs. The plan is being developed by and the experiments necessary to determine the feasibility of its implementation are being conducted by scientists from the National Health and Environmental Effects Research Laboratory, the National Risk Management Research Laboratory, the National Exposure Research Laboratory and the National Center for Environmental Assessment.

Monarca, S., Richardson, S.D., Feretti, D., Grottolo, M., Thruston, Jr., A.D., Zani, C., Navazio, G., Ragazzo, P., Zerbini, I., and Alberti, A. Mutagenicity and disinfection by-products in surface drinking water disinfected with peracetic acid. Environmental Toxicology and Chemistry 21 (2):309-318 (2002). EPA/600/J-02/136.

2/1/2002

**Contact:** Susan D. Richardson

**Abstract:** The aims of this research were to study the influence of peracetic acid (PAA) on the formation of mutagens in surface waters used for human consumption and to assess its potential application for the disinfection of drinking water. The results obtained using PAA were compared to those found with sodium hypochlorite (NaClO) and chlorine dioxide (ClO<sub>2</sub>). The Ames test, root anaphase aberration assay, and root/micronuclei assay in *Allium cepa* and *Tradescantia*/micronuclei test were used to evaluate the mutagenicity of disinfected samples. Micro biological tests were also performed, and disinfection by-products (DBPs) were identified using gas chromatography/mass spectrometry (GC/MS). A slight bacterial mutagenicity was found in raw lake and river water, and similar activity was detected in disinfected samples. A plant test revealed genotoxicity in raw river water, and microbiological analysis showed that PAA has bactericidal activity but lower than that of the other disinfectants. The DBPs produced by PAA were mainly carboxylic acids, which are not recognized as mutagenic, whereas the waters treated with the other disinfectants showed the presence of mutagenic/carcinogenic halogenated DBPs. However, additional experiments should be performed with higher concentrations of PAA and using water with higher organic carbon content to better evaluate this disinfectant.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Richardson, S.D. The role of GC-MS and LC-MS in the discovery of drinking water disinfection by-products. Journal of Environmental Monitoring 4 (1):1-9 (2002). EPA/600/J-02/132.

1/28/2002

**Contact:** Susan D. Richardson

**Abstract:** Gas chromatography-mass spectrometry (GC-MS) has played a pivotal role in the discovery of disinfection by-products (DBPs) in drinking water. DBPs are formed when disinfectants, such as chlorine, ozone, chlorine dioxide or chloramine, react with natural organic matter in the water. The first DBP known chloroform was identified by Rook in 1974 using GC-MS. Soon thereafter, chloroform and other trihalomethanes were found to be ubiquitous in chlorinated drinking water. In 1976, the National Cancer Institute published results linking chloroform to cancer in laboratory animals, and an important public health issue was born. Mass spectrometry and, specifically, GC-MS became the key tool used for measuring these DBPs in water and for discovering other DBPs that were formed. Over the last 25 years, hundreds of DBPs have been identified, mostly through the use of GC-MS, which has spawned additional health effects studies and regulations. Early on, GC with low resolution electron ionization (EI)-MS was used, together with confirmation with chemical standards, for identification work. Later, researchers utilized chemical ionization (CI)-MS to provide molecular weight information and high resolution EI-MS to aid in the determination of empirical formulae for the molecular ions and fragments. More recently, liquid chromatography-mass spectrometry (LC-MS) with either electrospray ionization (ESI) or atmospheric pressure chemical ionization (APCI) has been used to try to uncover highly polar DBPs that most experts believe have been missed by earlier GC-MS studies. Despite 25 years of research in the identification of new DBPs, new ones are being discovered every year, even for chlorine which has been the most extensively studied.

Jan 1, 2002 - Dec 31, 2002

*Presented Published*

Richardson, S.D., Simmons, J.E., and Rice, G. Disinfection Byproducts: the next generation. Environmental Science & Technology 36 (9):198A-205A (2002). EPA/600/J-03/365.

5/1/2002

**Contact:** Susan D. Richardson

**Abstract:** Disinfection of drinking water is rightly hailed as a major public health triumph of the 20th Century. Before widespread disinfection of drinking water in the U.S. and Europe, millions of people died from infectious waterborne diseases, such as typhoid and cholera. The microbial pathogens causing these diseases were the targets of chemical disinfection of drinking water beginning in the early 1900s, and those deaths attributable to these waterborne pathogens virtually ceased in developed nations (1). Recent large outbreaks of waterborne illness (cryptosporidiosis in Milwaukee in 1993 and cholera in Peru beginning in 1991) served as dramatic reminders of the need to properly disinfect and control waterborne pathogens in drinking water and suggested the need to continually reevaluate disinfection techniques to improve/ensure drinking water disinfection. This recognition has led to research and use of alternative disinfectant strategies. While pathogenic organisms provide the primary human health risk from drinking water, chemical disinfection by-products (DBPs) also provide an unintended health hazard. Disinfectants, in addition to effectively killing harmful microorganisms, are powerful oxidants and oxidize the organic matter naturally present in most source waters (rivers, lakes, and many groundwaters), forming DBPs. Chlorine, ozone, chlorine dioxide, and chloramine are the most popular disinfectants in use today, and each produces its own suite of chemical DBPs in drinking water (2). Most developed nations have created regulations or guidelines to control DBPs in order to minimize consumers' exposure to hazardous chemical DBPs, while at the same time, maintaining adequate disinfection and control of targeted pathogens. As such, developed nations often have the opportunity to evaluate the nature and the magnitude of human health risks posed by DBPs and implement changes in drinking water treatment when necessary. Despite much research on drinking water DBPs over the last several years, we have only been aware of them since the early 1970s. In 1974, Rook reported the identification of the first DBPs--chloroform and the other trihalomethanes (THMs)--that are formed in chlorinated drinking water (3). In 1976, the U.S. Environmental Protection Agency (EPA) published the results of a national survey which showed that chloroform and the other THMs were ubiquitous in chlorinated drinking water (4). In the same year (1976), the National Cancer Institute published results linking chloroform to cancer in laboratory animals (5). As a result, an important public health issue was born. In 1979, the U.S. EPA issued a regulation to control THMs at 100 micrograms/L (ppb) in drinking water (6); and in 1998, the Stage 1 Disinfectants/Disinfection By-products (D/DBP) Rule was promulgated, which lowered permissible levels of THMs to 80 micrograms/L and regulated five of the haloacetic acids (HAAs), bromate, chlorate, and chlorite for the first time (Table 1) (7). The Stage 1 D/DBP Rule became effective 3 years following the promulgation of the Rule (2001). With stricter regulations on THMs and new regulations on HAAs, many drinking water utilities are having to change from chlorine to alternative disinfectants (including ozone, chlorine dioxide, and chloramine) to meet the new regulations. However, new issues and problems can result. For example, the use of ozone can significantly reduce (or eliminate) the formation of THMs and HAAs, but can increase the formation of bromate, when elevated levels of bromide are present in source waters. In the almost 30 years since the THMs were identified, DBPs have been actively investigated. Significant research efforts have been directed toward increasing our understanding of DBP formation, occurrence, and health effects. However, although approximately 500 DBPs have been reported in the literature (2), only a small number have been addressed either in quantitative occurrence or health effects studies. The DBPs that have been quantified in drinking water are generally present at low to mid-ppb (micrograms/L) levels. However, more than 50% of the total organic halide (TOX) formed in the chlorination of drinking water is still quantitatively unaccounted for (8), and nothing is known about the potential toxicity of many of the DBPs present in drinking water. Much of the previous health effects research directed toward understanding the effects of chronic exposure to DBPs has focused on cancer and/or mutagenicity. Today, there are new, additional concerns about potential reproductive and developmental effects, and it is now recognized that the currently available single-chemical toxicity studies cannot by themselves explain epidemiologic effects observed in human populations, necessitating the toxicologic study of DBP mixtures. Also, other routes of exposure besides ingestion are now being recognized as significant. For example, recent work by researchers at Health Canada has revealed that a person can receive twice the exposure to THMs through showering (by inhalation) and equivalent exposure through dermal absorption (bathing, washing clothes, etc.) as ingesting 2 liters of water (9). In addition, new human exposure work is being conducted in which blood and urine are being monitored for DBP exposures (10-14). New work is also being conducted to try to uncover the missing fraction of DBPs' (e.g., the >50% TOX not identified in chlorinated drinking water and the >60% of assimilable organic carbon not being identified in ozonated drinking water). Progress is being made in the identification of highly polar, high molecular weight, and other DBPs that have been missed previously. As a result of all these new efforts, DBP research is entering into an entirely new phase ('The Next Generation'). No longer is cancer the only health endpoint detected in epidemiologic studies. No longer are THMs the only DBPs considered for quantitative occurrence studies or toxicity/epidemiologic studies/risk assessments. As researchers continue to tackle this important public health issue, exciting new work is taking place. The article will discuss this next wave of research and the information that can be gained by it.

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*Presented Published*

Arbuckle, T.E., Hrudey, S.E., Krasner, S.W., Nuckols, J.R., Richardson, S.D., Singer, P.C., Mendola, P., Dodds, L., Weisel, C.E., Ashley, D.L., Froese, K.L., Pegram, R.A., Schultz, I.R., Reif, J., Bachand, A.M., Benoit, F.M., Lynberg, M.C., Poole, C., and Waller, K. Assessing exposure in epidemiologic studies to disinfection by-products in drinking water: report from an international workshop. *Environmental Health Perspectives* 110 (1):53-60 (2002). EPA/600/J-03/149. 2/2/2002

**Contact:** Susan D. Richardson

**Abstract:** The inability to accurately assess exposure has been one of the major shortcomings of epidemiologic studies of disinfection by-products (DBPs) in drinking water. A number of contributing factors include: (1) limited information on the identity, occurrence, toxicity and pharmacokinetics of the many DBPs that can be formed from chlorine, chloramine, ozone, and chlorine dioxide disinfection; (2) the complex chemical inter-relationships between DBPs and other parameters within a municipal water distribution system; and (3) difficulties obtaining accurate and reliable information on personal activity and water consumption patterns. In May 2000, an international workshop was held to bring together various disciplines to develop better approaches for measuring DBP exposure for epidemiologic studies. The workshop reached consensus about the clear need to involve relevant disciplines (e.g., chemists, engineers, toxicologists, biostatisticians and epidemiologists) as partners when developing epidemiologic studies of DBPs in drinking water. The workshop concluded that greater collaboration of epidemiologists with water utilities and regulators should be encouraged to promote making regulatory monitoring data more useful for epidemiologic studies. Likewise, exposure classification categories in epidemiologic studies should be chosen to make results useful for regulatory or policy decision-making.

Chen, P.H., Richardson, S.D., Krasner, S.W., Majetich, G., and Glish, G. Hydrogen abstraction and decomposition of bromopicrin and other trihalogenated disinfection by-products by GC/MS. *Environmental Science & Technology* 36 (15):3362-3371 (2002). EPA/600/J-03/153. 8/15/2002

**Contact:** Susan D. Richardson

**Abstract:** Tribromonitromethane (bromopicrin), dibromochlorani-tromethane, bromodichloronitromethane, and trichloroni-tromethane (chloropicrin) have been identified as drinking water disinfection byproducts (DBPs). They are thermally unstable and decompose under commonly used injection port temperatures (200-250 degrees C) during gas chromatography (GC) or GC/mass spectrometry (GC/MS) analysis. The major decomposition products are haloforms (such as bromoform), which result from the abstraction of a hydrogen atom from the solvent by thermally generated trihalomethyl radicals. A number of other products formed by radical reactions with the solvent and other radicals were also detected. The trihalonitromethanes also decompose in the hot GC/MS transfer line, and the mass spectra obtained are mixed spectra of the undecomposed parent compound and decomposition products. This can complicate the identification of these compounds by GC/MS. Trihalomethyl compounds that do not have a nitro group, such as tribromoacetonitrile, carbon tetrabromide, methyl tribromoacetate, and tribromoacetaldehyde, do not decompose or only slightly decompose in the GC injection port and GC/MS transfer line. The brominated trihalomethyl compounds studied also showed H/Br exchange by some of their fragment ions. This H/Br exchange also makes the identification of these compounds in drinking water more difficult. The extent of H/Br exchange was found to depend on the mass spectrometer ion source temperature, and it is proposed that the internal surface of the ion source is involved in this process.

Richardson, S.D. Environmental mass spectrometry: emerging contaminants and current issues. *Analytical Chemistry* 74 (12):2719-2742 (2002). EPA/600/J-03/154. 6/15/2002

**Contact:** Susan D. Richardson

**Abstract:** This review covers developments in environmental mass spectrometry over the period of 2000-2001. A few significant references that appeared between January and February 2002 are also included. The previous Environmental Mass Spectrometry review was very comprehensive, including more than 500 references. This year, however, *Analytical Chemistry* has changed its approach to include only 100-200 significant references, and to mainly focus on trends in analytical methods. As a result, this year the review will limit its focus to new, emerging contaminants and environmental issues that are driving most of the current research. Even with a more narrow focus, only a small fraction of the quality research publications could be discussed. Thus, this review will not be comprehensive, but will highlight new areas and discuss representative papers in the areas of focus.

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*Presented Published*

Collette, T.W., and Williams, T.L. The role of Raman spectroscopy in the analytical chemistry of potable water. Journal of Environmental Monitoring 4 (1):27-34 (2002). EPA/600/J-02/135.

1/15/2002

**Contact:** Timothy W. Collette

**Abstract:** Advances in instrumentation are making Raman spectroscopy the tool of choice for an increasing number of chemical applications. For example, many recalcitrant industrial process monitoring problems have been solved in recent years with in-line Raman spectrometers. Raman is attractive for these applications for many reasons, including remote noninvasive sampling, minimal sample preparation, and tolerance of water. To a lesser extent, Raman spectroscopy is beginning to play a significant role in environmental analysis for the same reasons. At present, the environmental applications typically apply only to the most contaminated situations, due to still relatively high limits of detection. However, some emerging sampling technologies hold out the promise that Raman may soon be more widely applicable to the analytical chemistry of potable water. Herein we discuss these recent advances, summarize some examples of environmental applications to aqueous systems, and suggest avenues of future developments that we expect to be most useful for potable water analysis. Also, a simplified, but detailed, theory of normal Raman scattering is presented. While resonance enhanced Raman spectroscopy, surface enhanced Raman spectroscopy, and nonlinear Raman techniques are briefly discussed, their theories and instrumental configurations are not addressed. Also, this article deals primarily with the modern dispersive Raman experiment (as opposed to the Fourier-transform Raman experiment), because it seems most suited for potable water analysis. The goal of this article is to give the environmental scientist with no specialized knowledge of the topic just enough theory and background to evaluate the utility of this rapidly developing analytical tool.

Hussein, M., Jin, M., and Weaver, J.W. Development and verification of a screening model for surface spreading of petroleum. Journal of Contaminant Hydrology 57 (3-4):281-302 (2002). EPA/600/J-03/069.

8/15/2002

**Contact:** James W. Weaver

**Abstract:** Overflows and leakage from aboveground storage tanks and pipelines carrying crude oil and petroleum products occur frequently. The spilled hydrocarbons pose environmental threats by contaminating the surrounding soil and the underlying ground water. Predicting the fate and transport of these chemicals is required for environmental risk assessment and for remedial measure design. The present paper discusses the formulation and application of the Oil Surface Flow Screening Model (OILSFSM) for predicting the surface flow of oil by taking into account infiltration and evaporation. Surface flow is simulated using a semi-analytical model based on the lubrication theory approximation of viscous flow. Infiltration is simulated using a version of the Green and Ampt infiltration model, which is modified to account for oil properties. Evaporation of volatile compounds is simulated using a compositional model that accounts for the changes in the fraction of each compound in the spilled oil. The coupling between surface flow, infiltration and evaporation is achieved by incorporating the infiltration and evaporation fluxes into the global continuity equation of the spilled oil. The model was verified against numerical models for infiltration and analytical models for surface flow. The verification study demonstrates the applicability of the model.

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*Presented Published*

Johnston, J.M., and Crossley, Jr., D.A. Forest ecosystem recovery in the southeast US: soil ecology as an essential component of ecosystem management. Forest Ecology and Management 155 (1-3):187-203 (2002). EPA/600/J-02/134.

1/1/2002

**Contact:** John M. Johnston

**Abstract:** The forestry industry in the southeastern United States relies upon soils that are highly eroded and depleted of their original organic matter and nutrient content. Pro-active land management can ensure continued and possibly increased production and revenue through the management and recovery of the soil resource. With an emphasis on loblolly pine (*Pinus taeda* L.) forests, this review integrates land-use history, pine ecology, silviculture, soil ecological research and the implications for forest management into a single discussion. Promoting soil recovery involves knowledge of ecosystem history and disturbance as well as nutrient cycling mechanisms, pools, fluxes and soil forming factors. Research on the rhizosphere is an area that is needed. Recovery of regional soils may confer benefits of drought and disease resistance. The goal of sustainable forestry is compatible with soil recovery; however, the technology and practices of modern forestry deserve thorough evaluation. Emphasis on the continued production of commodities, the agricultural model, is much different from managing for the functioning of healthy forest ecosystems. Many of the practices and outcomes of intensive forest management, including short rotations, harrowing, subsoiling, and burning or removal of logging slash, seem to be at odds with the goal of soil recovery. Best management practices that foster soil recovery include less intensive stand utilization and reduced soil disturbance. Stem-only harvest and longer rotations permit a recovery of soil biodiversity and an accrual of detritus and soil organic matter. Windrowing and similar techniques have dramatic and lasting effects on soil development. No-tillage agriculture as a model for pine plantations is discussed.

## RESEARCH RPT

Weinberg, H.S., Krasner, S.W., Richardson, S.D., and Thruston, Jr., A.D. The occurrence of disinfection by-products of health concern in drinking water: results of a nationwide DBP occurrence study. 2002. EPA/600/R-02/068 (NTIS PB2003-106823).

9/30/2002

**Contact:** Susan D. Richardson

**Abstract:** The motivation for this Nationwide Disinfection By-product (DBP) Occurrence Study was two-fold: First, more than 500 DBPs have been reported in the literature, yet there is almost no quantitative occurrence information for most. As a result, there is significant uncertainty over the identity and levels of DBPs that people are exposed to in their drinking water. Second, only a limited number of DBPs have been studied for adverse health effects. So, it is not known whether other DBPs (besides the few that are currently regulated) pose a risk to human health. To determine whether other DBPs pose an adverse health risk, more comprehensive quantitative occurrence and toxicity data are needed. Because health effects studies are very expensive, it is not possible to test all DBPs that have been reported. It is also not feasible to measure >500 DBPs in waters across the United States. Thus, results of a DBP prioritization effort by scientists at the U.S. Environmental Protection Agency (USEPA) Office of Water and the USEPA Office of Prevention, Pesticides, and Toxic Substances were used to focus this study on those DBPs that were the most toxicologically significant. These EPA experts applied an in-depth mechanism-based structural activity relationship analysis to the more than 500 DBPs reported in the literature, supplemented by an extensive literature search for genotoxicity and other data, and ranked the carcinogenic potential of these DBPs. Approximately 50 DBPs that received the highest ranking for potential toxicity and that were not included in the USEPA's Information Collection Rule (ICR) were selected for this occurrence study. These DBPs, denoted as 'high priority' DBPs in this report, included such compounds as MX [3-chloro-4-(dichloromethyl)-5-hydroxy-2(5H)-furanone], brominated forms of MX (BMXs), halonitromethanes, iodo-trihalomethanes, and many brominated species of halomethanes, haloacetonitriles, halo ketones, and haloamides.



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*Presented Published*

*SYMPOS/CONF*

Bird, S.L., Harrison, J., Exum, L.R., Alberty, S.W., and Perkins, C. Screening to identify and prevent urban storm water problems: estimating impervious area accurately and inexpensively. 2002 National Water Quality Monitoring Council Conference, Madison, WI, May 20-23, 2002. 2002. EPA/600/A-03/024 (NTIS PB2003-106604), <http://www.nwqmc.org/NWQMC-Proceedings/Papers-Alphabetical%20by%20First%20Name/Jim>

5/23/2002

**Contact:** Sandra L. Bird

**Abstract:** Complete identification and eventual prevention of urban water quality problems pose significant monitoring, "smart growth" and water quality management challenges. Uncontrolled increase of impervious surface area (roads, buildings, and parking lots) causes detrimental hydrologic changes, stream channel erosion, habitat degradation and severe impairment of aquatic communities. Existing aerial photography (digital orthophoto quarter quadrangles - DOQQ's), sampled statistically using desktop GIS tools, was used to evaluate impervious area estimates based on readily available landscape data including: categorized land-cover data (National Land Cover Data - NLCD); block-level census data; and road networks. Models linking the photo interpretation and wide area estimation techniques provided: 1) cheap estimates of impervious cover with known accuracy at the watershed and sub-watershed scales; 2) a comprehensive state-wide ranking of Georgia waters likely impaired or threatened by urban storm water; and 3) characterization of change in imperviousness over time. Multiple data source estimation of imperviousness provides improved accuracy compared to the use of land-use/land-cover alone, especially for the 5-10% impervious range where prevention of storm water problems is critical. Estimated imperviousness change from 1993 to 1999 revealed 51 Georgia watersheds defined by 12-digit hydrological unit codes (HUCs) with substantial impervious area increases (class changes) during this short, 6-year period. For 1999, 92 HUCs were estimated to be more than 10% impervious with potentially detrimental aquatic impacts, and 137 in the 5 to 10% range with detrimental aquatic impacts likely with future growth unless preventive actions are taken. Similar analyses will be expanded to the 8 Southeastern states of EPA Region 4. These screening results can guide in-situ monitoring to confirm problems, aid listing of impaired waters under Section 303(d) of the Clean Water Act and total maximum daily load (TMDL) development, provide reliable scientific information to energize sound local planning and land-use decisions, and promote protection and restoration of urban streams.

Frick, W.E., Baumgartner, D.J., Denton, D.L., and Roberts, P.J.W. New developments of Visual Plumes - evaluation of bacterial pollution. Presented at: 2nd International Conference on Marine Waste Water Discharges, Istanbul, Turkey, September 16-20, 2002. EPA/600/A-03/025.

9/16/2002

**Contact:** Walter E. Frick

**Abstract:** Virulent or innocuous, high bacteria concentrations can force health authorities to close beaches, to the regret of the public and the communities that depend on the tourist trade for their livelihood. But, with real-time identification and measurement still in the future, often, by the time the incident has occurred, the potential danger has passed and perfectly safe beaches go unenjoyed (as many tests are based on harmless indicator bacteria). Instead, if reliable predictive models could be developed to accurately predict surfzone bacterial concentrations, the number of beach closures might be reduced significantly. Monitoring would serve the role of assuring model efficacy. The U.S. EPA Visual Plumes model is used to demonstrate how such a modeling system may ultimately function. It is also used to identify potential engineering practices, such as port design, to achieve greater rise to optimize the antiseptic effect of sunlight; to minimize nearshore impacts. Areas for immediate model improvement are identified and related potential health issues, such as toxics, are discussed.

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Weaver, J.W., Tebes-Stevens, C.L., and Wolfe, K. Uncertainty in model predictions-plausible outcomes from estimates of input ranges. Presented at: Brownfields 2002, Charlotte, NC, November 13-15, 2002. EPA/600/A-03/021.

11/13/2002

**Contact:** James W. Weaver

**Abstract:** Models are commonly used to predict the future extent of contamination given estimates of hydraulic conductivity, porosity, hydraulic gradient, biodegradation rate, and other parameters. Often best estimates or averages of these are used as inputs to models, which then transform them into output concentrations. Despite this evident certainty, all properties of the subsurface are both uncertain, because of imperfect measurement methods, and subject to point-to-point variability, because of geologic heterogeneity. Where used as purely predictive tools (i.e., in the absence of model calibration to field data), uncertainty and variability lead to the need for assessment of the plausible range of model outcomes. For Brownfields sites, the need to provide rapid assessment of contamination may not allow extensive field and modeling studies, where calibration data sets would be obtained. In those and other cases there is a need for evaluation of model uncertainty given input variation. Our approach is to use all combinations of input parameters to determine the earliest and latest first arrivals, the lowest and highest peak concentration, the shortest and longest duration of contamination, and the lowest and highest risk scenarios. Results of simulations show that even moderate ranges of input variation generate significant differences in model predictions. These differences are greater than obtained from simple one parameter at a time uncertainty analyses, because of combined influences of multiple parameters. For example, hydraulic conductivity, porosity and gradient together determine the seepage velocity, and variation of each of parameter needs to be considered in order to determine the extremes of velocity. The extreme parameter sets were found to be different for some of the four predicted model outputs (first arrival, maximum concentration, duration, risk). This result shows that selection of worst case parameter set depends on the desired output of the model. The simulations showed that the best and worst case parameter sets for first arrival time, maximum concentration and duration were consistent across all simulations and could thus be selected a priori. Those for risk, however, could be determined only by performing an uncertainty analysis for each input parameter set.

Weaver, J.W., and Small, M.C. MTBE is a little bit ok?. Presented at: National Groundwater Association Petroleum Hydrocarbons Conference, Atlanta, GA, November 6-8, 2002. EPA/600/A-03/022.

11/6/2002

**Contact:** James W. Weaver

**Abstract:** Methyl tertiary butyl ether (MTBE) has been used as a gasoline additive to serve two major purposes. First, MTBE was used as an octane-enhancer to replace organic lead, beginning in about 1979. Beginning in about 1992, MTBE was also used as a fuel oxygenate additive to meet requirements of the Clean Air Act Amendments (CAAA) of 1990. Generally, the amount of MTBE used for octane enhancement was lower than that required to meet CAAA requirements. An unintended consequence of using MTBE to address air quality issues has been widespread groundwater contamination. The decision to use certain amounts of MTBE or other chemicals as gasoline additives is the outcome of economic, regulatory, policy, political, and scientific considerations. Decision makers ask questions such as "How do ground water impacts change with changing MTBE content? How many wells would be impacted? and What are the associated costs?" These questions are best answered through scientific inquiry, but many different approaches could be developed. Decision criteria include time, money, comprehensiveness, and complexity of the approach. Because results must be communicated to a non-technical audience, there is a trade-off between the complexity of the approach and the ability to convince economists, lawyers and policy makers that the results make sense. The questions on MTBE content posed above were investigated using transport models, a known release scenario and varying gasoline compositions. A set of simulations was performed that assumed 3% (octane enhancement) and 11% (CAAA) MTBE in gasoline. The results were that ground water concentrations would be reduced in proportion to the reduction of MTBE in the fuel. Plume lengths, though, would not be proportionately reduced. One implication of these results was that the concentrations would be reduced, but the number of impacted wells would remain similar. Because simulations included emplacement of the gasoline, dissolution from contact with flowing ground water and transient transport in the aquifer, a common sense explanation of the results was difficult to construct. A simpler model was then used for the purpose of explaining to policy makers why the plume length reductions were less than proportionate to the reduction of the amount of MTBE. The model was simple enough (one-dimensional, steady state, constant source concentration) so that the effect of each term of the transport equation on plume length could be easily shown. The weight of evidence from using multiple models, direct explanations from the transport equation, and field observation, should provide a sufficient basis for policy makers to understand scientifically how gasoline composition affects ground water impacts.

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Rashleigh, B. Ecological endpoint modeling for TMDLs: effects of sediment on fish populations.  
Presented at: National Total Maximum Daily Loads Science and Policy Conference, Phoenix, AZ,  
November 13-16, 2002. EPA/600/A-03/020.

11/13/2002

**Contact:** Brenda Rashleigh

**Abstract:** Sediment is one of the primary stressors of concern for Total Maximum Daily Loads (TMDLs) for streams, and often it is a concern because of its impact on ecological endpoints. A modeling approach relating sediment to stream fish population dynamics is presented. Equations are developed to characterize effects of sediment on survival and reproduction, and these vital rates are incorporated into an age-structured population matrix model. The matrix model can be used to calculate the long-term population growth rate, and to project population dynamics. An example application for a darter species, a species that is likely to be most sensitive to sediment impacts, is presented. This approach can be used in TMDL development: a target sediment level may be set based on the criterion that the long term fish population growth-rate is positive, and a margin of safety can be estimated by including variability in the matrix model. Models that simulate the response of ecological endpoints to sediment can provide additional management approaches for impaired streams.